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On the Isotope Corrections in Molecular Spectra

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According to the simple theory of the rigid rotator and harmonic oscillator, the coefficients of $J(J+1)$ and $(v+\frac{1}{2})$ in the energy should be inversely proportional to respectively the reduced mass and the square root thereof. Actually various small corrections, important only in compounds containing hydrogen or deuterium, make the mass dependence slightly different, and hence, at least in principle, explain why spectroscopic observations may yield slightly incorrect mass ratios for isotopes. The corrections are due to four causes (a) anharmonicity, (b) interaction between vibration and electronic motion even when perturbations between different electronic states are neglected, (c) L uncoupling or in other words perturbations between states differing by one unit in Λ, (d) interaction between states of equal Λ. The formulas for the various corrections are collected—some old, some new or more exact than previously. The relative magnitudes of the different effects are estimated. Incidentally, perturbations between states of equal Λ are studied in general. They should increase in intensity with the vibrational quantum number v, all other things being equal, in contrast to the perturbations due to L uncoupling, which increase with J. The electronic isotope shift, or displacement in the absolute value of the energy is also treated. Here the correction for the motion of the center of gravity of the molecule, usually neglected, is shown to be fully coordinate in importance with other terms. Shifts for ultraviolet lines of hydrogen are calculated with the Wang wave functions, and agree qualitatively with experiment. A concluding section is included on the mean square angular momentum of H_2, which enters in connection with diamagnetism and the Stern-Gerlach effect.

THE observed energies of singlet states of diatomic molecules are ordinarily represented by a formula

$$W=W_0^*+h\omega^*(v+\tfrac{1}{2})+B^*J(J+1)+\cdots, \quad (1)$$

where v and J, are respectively, the vibrational and rotational quantum numbers. The coefficients ω^*, B^*, however, do not have exactly the ideal values

$$\omega_0=(1/2\pi)(a/M)^{\frac{1}{2}}, \quad B_0=h^2/8\pi^2Mr_0^2 \quad (2)$$

characteristic of the harmonic oscillator and rigid rotator respectively. The notation M is used for the reduced mass $M_1M_2/(M_1+M_2)$; r_0 is the equilibrium internuclear distance for an irrotational molecule devoid of centrifugal distortion, and a is identified with the coefficient of the first term of the usual expansion

$$E_n(r)=W_0+\tfrac{1}{2}ar_0^2(\xi^2+a_1\xi^3+a_2\xi^4+\cdots) \quad (3)$$

of the radial potential energy. Here $\xi=(r-r_0)/r_0$.

Let primes and double primes refer to two different isotopes. Both theoretically and empirically, the ratios $\omega^{*\prime}/\omega^{*\prime\prime}$ and $(B^{*\prime}/B^{*\prime\prime})^{\frac{1}{2}}$ deviate slightly from the simple value

$$\omega_0'/\omega_0''=(B_0'/B_0'')^{\frac{1}{2}}=(M''/M')^{\frac{1}{2}} \quad (4)$$

obtained from (2). There are many small corrections which cause B^*, ω^* to differ from B_0, ω, and which hence make the apparent isotope ratios, as revealed by band spectra, somewhat different from (4). The literature is in a rather confused state regarding their number and

[1] A preliminary account of the present paper was given at the St. Louis meeting of the Am. Phys. Soc., Phys. Rev. 49, 417 (1936).

nature. The purpose of the present paper is to summarize the various correction terms which have been given to date, and especially to present certain additional terms which appear to have previously been overlooked although they may be as large as the others. We must, however, not fail to mention that notable theoretical work on isotope corrections has recently been published by Dieke, and the approximations which he makes are adequate in the examples which he studies. To avoid undue complication, we throughout confine our attention to singlet states.

The corrections are all sufficiently small that they may be considered additive. In other words, if (a) is some effect which, taken by itself, makes B^* acquire a value $B_0(1+\gamma_a)$ different from (2), and if there are other disturbing influences (b), (c), (d), the final formula is

$$B^*=B_0(1+\gamma_a+\gamma_b+\gamma_c+\gamma_d)=B_0(1+\gamma). \quad (5)$$

Similarly we can take

$$\omega^*=\omega_0[1+\delta_a+\delta_b+\delta_c+\delta_d]=\omega_0[1+\delta]. \quad (6)$$

The apparent isotope ratio $(B^{*\prime}/B^{*\prime\prime})^{\frac{1}{2}}$ in the rotational case should differ from (4) by a factor $1+\frac{1}{2}\gamma'-\frac{1}{2}\gamma''$. In the vibrational isotope effect, the analogous relation is

$$\omega^{*\prime}/\omega^{*\prime\prime}=(M''/M')^{\frac{1}{2}}(1+\delta'-\delta'').$$

The value of δ is not in general the same as that of $\frac{1}{2}\gamma$. Hence the correction factor to (4) is unlike for rotation and vibration. The reason that γ' differs from γ'', or δ' from δ'', is that γ, δ are functions of the nuclear masses. Since γ, δ are themselves very small quantities, the expressions $\gamma'-\gamma''$ and $\delta'-\delta''$ will be quite negligible unless the ratio of the reduced masses for the two isotopes differs markedly from unity. Hence all the corrections which we discuss are important only when the pair of isotopes is a hydride and a deuteride. In fact, it is only the discovery of deuterium that makes most of the present paper of other than academic interest.

We may distinguish between four effects (a), (b), (c), (d), all of which make the empirical isotope ratios differ from the ideal values (4).

(a) Anharmonicity

Even for a vibrator-rotator, involving only nuclear in distinction from electronic coordinates, there will be departures from (4) if the restoring forces are not simple harmonic. The resulting modifications have been studied particularly by Dunham[2] and Crawford.[3] Dunham's formulas show that

$$\gamma_a=(B_0^2/2\omega_0^2)[15+41a_1-9a_2+15a_3-23a_1a_2+21(\tfrac{1}{2}a_1^2+\tfrac{1}{2}a_1^3)], \quad (7)$$

$$\delta_a=(B_0^2/32\omega_0^2)(200a_4-380a_1a_3-134a_2^2+459a_1^2a_2), \quad (8)$$

with $a_1\cdots a_4$ as in (3).

(b) Diagonal Elements

All perturbation calculations on diatomic molecules start with a set of initial wave functions Ψ in which the nuclear and electronic variables are separated, so that[4]

$$\Psi=\Phi_n(x_1,\cdots,z_f,r)R_{nv}(r)u_{J\Lambda}(\theta,\varphi)f(X,Y,Z). \quad (9)$$

Here Φ_n is a function of the coordinates $x_1\cdots z_f$ of the electrons relative to the center of gravity as origin; R_{nv} depends only on the internuclear distance r, and $u_{J\Lambda}$ is a symmetrical top function which involves merely the angular variables θ, φ specifying the spatial orientation of the molecular axis. The function f depends only on the coordinates X, Y, Z of the center of gravity, and has the usual plane wave exponential form. The factor Φ_n contains r as a parameter, and satisfies the wave equation

$$[\mathbf{H}-E_n(r)]\Phi_n=0 \quad (10)$$

for "clamped nuclei." The eigenvalue of (10) for a given state n involves r parametrically, and is the same as the radial potential function (3). It is usually assumed that the differential equation

[2] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[3] F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **47**, 931 (1935).
[4] R. de L. Kronig, *Band Spectra and Molecular Structure*, p. 42; or J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

satisfied by R_{nv} is that of a system of one degree of freedom with the potential (3) supplemented by the ordinary centrifugal term $[J(J+1)-\Lambda^2]h^2/8\pi^2Mr^2$. This supposition, however, is not quite right. Instead the wave equation appropriate to R_{nv} is

$$(-h^2/8\pi^2M9)(d^2R_{nv}/dr^2)+[E_n(r)+P_{nn}+Q_{nn}+S_{nr}+(J^2+J-\Lambda^2)h^2/8\pi^2Mr^2]R_{nv}-WR_{nv}=0, \quad (11)$$

where
$$P_{n'n}(r)=(h^2/8\pi^2Mr^2)\Xi_{n'n} \quad \text{with} \quad \Xi_{n'n}=\int\cdots\int\Phi_{n'}{}^{\dagger}(\mathbf{P}_x{}^2+\mathbf{P}_y{}^2)\Phi_n d\tau, \quad (12)$$

$$Q_{n'n}(r)=(h^2/8\pi^2M)\int\cdots\int-\Phi_{n'}{}^{\dagger}\partial^2\Phi_n/\partial r^2 d\tau. \quad (13)$$

The formula for S_{nn} is furnished later in Eq. (14). $d\tau$ is an abbreviation for the $3f$-dimensional volume element $dv_1\cdots dv_f$. In (12), $\mathbf{P}_x$ is the operator $i^{-1}\Sigma_k(y_k\partial\cdots/\partial z_k-z_k\partial\cdots/\partial y_k)$ which gives the electronic angular momentum about the x axis, measured in multiples of $h/2\pi$, while $\mathbf{P}_y$ is the corresponding operator for the y axis. It is assumed throughout that the z axis connects the nuclei. The dagger is used to denote the conjugate imaginary, and for present purposes we take $n'=n$. In writing (11), we have used a radial wave function normalized with respect to dr (rather than to r^2dr as in reference 4), for this procedure makes the formulas more compact.

The extra terms P_{nn}, Q_{nn} in (11) may be qualitatively described as representing coupling between vibration and electronic motion. They have already been given by Kronig and others.[4] The remaining additional term S_{nn} owes its origin to the fact that the center of gravity of the molecule does not quite coincide with the center of gravity of the nuclei, so that the latter wobbles about the former. This term does not appear to have been explicitly written down previously in connection with the radial equation, because it has commonly been assumed that the distinction between the two centers of gravity is of no account in view of the light mass of the electrons. However, we shall see later in the article that the S_{nn} term is often as important as the P_{nn}, Q_{nn} ones, and that all three should be considered as an organic whole in treating the coupling of electronic and nuclear motions. The formula for $S_{n'n}$ is

$$S_{n'n}(r)=-(h^2/8\pi^2M_{1+2})\int\cdots\int\Phi_{n'}{}^{\dagger}(\Sigma_i\nabla_i{}^2+2\Sigma_{j>i}\nabla_j\cdot\nabla_i)\Phi_n d\tau, \quad (14)$$

where M_{1+2} is the total mass M_1+M_2 of the two nuclei. The symbols ∇_i and $\nabla_i{}^2$ are respectively the gradient and Laplacian operators in the x_i, y_i, z_i space and we shall let ∇_{XYZ}, $\nabla^2{}_{XYZ}$ have similar significance in the X, Y, Z coordinate system.

To derive (14), we note that motion of the center of gravity introduces the term $-(h^2/8\pi^2M_{1+2})\nabla^2{}_{XYZ}$ in the Hamiltonian function. Despite the fact that Φ does not apparently contain X, Y, Z explicitly, $\nabla_{XYZ}\Phi$ does not vanish, as in differentiation with respect to X, Y, Z it must be supposed that the electronic coordinates are kept fixed in space rather than fixed relative to the nucleus. Hence when X is given a variation δX, one has $\delta X_1=\cdots=\delta X_n=-\delta X$ and so

$$-(h^2/8\pi^2M_{1+2})\nabla^2{}_{XYZ}\Psi=-(h^2/8\pi^2M_{1+2})Ru[\Phi_n\nabla^2{}_{XYZ}f-2\nabla_{XYZ}f\Sigma_i\nabla_i\Phi_n+f(\Sigma_i\nabla_i{}^2\Phi_n+2\Sigma_{j>i}\nabla_i\nabla_j\Phi_n). \quad (15)$$

To obtain (14), one integrates over the electronic coordinates in the usual way. The cross terms in $\nabla f\cdot\nabla\Phi_n$ in (15) vanish on integration in the diagonal case $n'=n$ because the mean momentum of the electrons relative to the center of gravity is zero. The first term of (15) merely governs the uniform motion of the center of gravity, and need not be considered for our purposes.

To proceed further, we develop $P_{nn}+Q_{nn}+S_{nn}$ as a Taylor's series

$$P_{nn}+Q_{nn}+S_{nn}=B_0[k_0+k_1\xi+k_2\xi^2+\cdots] \quad (16)$$

about the equilibrium position r_0 associated with (4). A perturbation calculation then shows that the resulting correction factors entering in (5) (6) are

$$\gamma_b=4k_1B_0{}^2/h^2\omega^2, \quad \delta_b=(2k_2-3k_1a_1)B_0{}^2/h^2\omega^2. \quad (17)$$

A simple proof of (17) is as follows: After the addition of the P_{nn}, Q_{nn}, S_{nn} and centrifugal terms, the equilibrium distance is no longer quite r_0, but is very approximately

$$r_0' = r_0 - (k_1 B_0/a r_0) + 2(B_0/a r_0) J(J+1) \tag{18}$$

as is seen by taking the minimum of the total effective potential in (11) and retaining only terms of lowest order. When we expand about the new equilibrium position, this potential becomes

$$W_0 + B_0[J(J+1)+k_0] + \tfrac{1}{2}(B_0^2/a r_0^2)[-k_1^2 + 4k_1 J(J+1) - 4J^2(J+1)^2] + \tfrac{1}{2}a(r-r_0')^2 + B_0 r_0^{-2}[k_2 + 3J(J+1) - \tfrac{1}{2}a_1(3k_1 - 6J^2 - 6J)](r_0 - r_0')^2 + \cdots. \tag{19}$$

In accordance with perturbation theory, we may replace $(r-r_0')^2$ by its mean value, which to a sufficient approximation[5] is the same as that of $(r-r_0)^2$ for the unperturbed motion. The latter is immediately obtained from the theorem that the mean kinetic and potential energies for a harmonic oscillator are each half the total energy, i.e.,

$$\tfrac{1}{2}a\overline{(r-r_0)^2} = \tfrac{1}{2}\overline{p_r^2}/M = \tfrac{1}{2}h\omega_0(v+\tfrac{1}{2}). \tag{20}$$

Thus $$W = W_0 + B_0[k_0 - (k_1 B_0/h\omega_0)^2] + B_0(1+\gamma_b)J(J+1) + h\omega_0(1+\delta_b)(v+\tfrac{1}{2}) + DJ^2(J+1)^2 - \alpha(v+\tfrac{1}{2})J(J+1), \tag{21}$$

where γ_b, δ_b are defined as in (17); and where

$$D = -4B_0^3/h^2\omega_0^2, \quad \alpha = -6(B_0^2/h\omega_0)(1+a_1). \tag{22}$$

Eqs. (17) are thus established. The formulas for D and α are the usual ones of the band spectroscopists for centrifugal expansion and the interaction of rotation and vibration.[6] As an incidental to our work, it is thus seen that the α, as well as, of course, the D term can be derived by a quite elementary perturbation calculation rather than, for instance, employing the Kratzer potential.[7] If we are interested in the effect of the various extra terms on the vibrational wave functions, this is, to a sufficient approximation, merely a shift in origin by an amount $r_0' - r_0$ given by (18).[8]

Eq. (21) does not contain higher powers than the first in $v+\frac{1}{2}$, as we have in (19) neglected terms of the third and higher orders in $(r-r_0')$ (also unimportant terms proportional to $(r_0'-r_0)^2(r-r_0)$ or $(r_0-r_0')^3$, etc., have been discarded in Eq. (19)). For most purposes, the coefficients of the higher powers of $v+\frac{1}{2}$ can be considered the same as when the extra terms in (11) are omitted. The coefficient of $v+\frac{1}{2}$ is slightly modified by the anharmonicity, essentially because v^m in the old quantum theory is replaced in the new mechanics by a polynomial in $v+\frac{1}{2}$ rather than simply $(v+\frac{1}{2})^m$. This is the Dunham-Crawford effect already included in (a).

In writing (19) and (21), we have not carried the development far enough to find the small correction factors to the coefficient of $(v+\frac{1}{2})J(J+1)$ which are comparable with those in (5)–(6) and which depend on the isotope. Further calculations, in which the equilibrium distance must be obtained more accurately than in (18), show that a more accurate value of this coefficient than α as given in (20) is[9]

$$\alpha^* = \alpha + (\alpha B_0^2/h^2\omega_0^2)[9a_1k_1 + (1+a_1)^{-1}(8k_1 - 2k_2 - 6a_1k_2 + 4k_3 - 8a_2k_1)].$$

The corresponding correction formula to the coefficient $-xh\omega_0$ of $(v+\frac{1}{2})$ is

$$(xh\omega)^* = xh\omega_0 + (4B_0^2x/h\omega_0)(12a_2 - 15a_1^2)^{-1}(-30a_3k_1 + 12k_4 - 12a_2k_2 + 78a_1a_2k_1 - 30a_1k_3 + 30a_1^2k_2 - 45a_1^3k_1).$$

In the present case $n'=n$, the expression Q_{nn} defined in (13) may be transformed into

$$Q_{nn}(r) = (h^2/8\pi^2M)\Theta_{nn} \quad \text{with} \quad \Theta_{nn} = \int\cdots\int |\partial\Phi_n/\partial r|^2 d\tau, \tag{23}$$

and is therefore positive. The relation (23) is proved from (13) by differentiating twice with respect to r the normalization integral

$$\int\cdots\int \Phi_{n'}{}^{\dagger}\Phi_n d\tau = \delta_{nn'}. \tag{24}$$

Eq. (24) is valid for all values of the parameter r since throughout the article we shall suppose the electronic wave functions normalized to unity regardless of the internuclear distance. The result (23) then follows immediately in the real case $\Phi_n{}^{\dagger} = \Phi_n$. If Φ_n is complex, the proof can still be carried through when use is made of the fact that without

[5] This statement does not contradict the fact that it is precisely the difference between r_0 and r_0' which causes the effects in question, as the shift in origin has eliminated first order expressions in $r-r_0'$, and the second-order terms need not be evaluated as accurately. In calculating $\alpha^*-\alpha$ it is necessary, however, to distinguish between the means of $(r-r_0)^2$ and of $(r-r_0')^2$.

[6] Cf., for instance, R. S. Mulliken, Rev. Mod. Phys. **1**, 67 (1930). In general we use the notation approved by Mulliken. His anharmonicity coefficients, however, relate to expansion about a Kratzer rather than harmonic potential, and so differ from ours. Thus his $-2b^*-2$ is the same as our a_1.

[7] The linear term in ξ in (16) or in the expansion of the centrifugal potential no longer vanishes when the potential is unsymmetrical. This is the physical reason why the cubic term a_1 in (3) contributes to the quadratic part of (19). Neglect of this contribution explains why Morse originally obtained an incorrect formula for α (Phys. Rev. **34**, 57 (1929)).

[8] Unless one is interested in extreme accuracy it is thus not necessary to resort to an elaborate perturbation calculation such as that of Pekeris (Phys. Rev. **45**, 98 (1934)).

[9] There are also modifications in α due to effects (a), (c), (d) and in $x\omega$ due to (a) and (d). Dunham[2] has treated (a). It can be shown that with the same hypotheses as in (28), (c) alters α by a factor

$$1 + B_0(5+6a_1)2(L^2+L)/3(1+a_1)h\nu(\Sigma;\ \Pi).$$

The correction formulas due to (d) involve $B_0/h\nu$, rather than $B_0^2/h^2\omega_0^2$ like (b). We shall not give their explicit form, since they are rather complicated and hard to use quantitatively as they require knowledge of the constants $\Omega^1_{nn'}$, $\Omega^2_{nn'}$ defined before (37).

loss of generality, Φ_n may be assumed to have the structure $F+iG$, where F, G are real and respectively even and odd with respect to reflection in some given plane containing the molecular axis. Consequently, F, $\partial F/\partial r$, $\partial^2 F/\partial r^2$ are all orthogonal to G, or derivatives thereof, and no cross terms in FG are involved in (24) or (13).

Furthermore, (14) may be transformed by partial integration into

$$S_{nn}(r)=(h^2/8\pi^2 M_{1+2})\int\cdots\int|\Sigma_i\nabla_i\Phi_n|^2 d\tau \tag{25}$$

and is also positive. There is no trouble in the complex case, as $\nabla_i F$ is orthogonal to $\nabla_i G$, and F to $\nabla_i{}^2 G$.

To simplify (17) it is customary to assume that Q_{nn}, S_{nn} are small compared with P_{nn} and to make use of the hypothesis of pure precession, in which the square of the total angular momentum is assumed to have a quantized value $L(L+1)$ like in an atom. Since in reality only the axial component Λ of electronic angular momentum is constant, this approximation is a crude one strictly allowable only in the limiting case of the "united atom" formed by coalescence of the nuclei. With the hypothesis of pure precession, the integral Ξ_{nn} in (12) has a value $L(L+1)-\Lambda^2$ independent of r, and then k_1, k_2 in (16) owe their existence (provided we disregard Q_{nn}, S_{nn}) entirely to the factor $1/r^2$ in (12). If we use (22), thus Eqs. (17) reduce to formulas

$$\left.\begin{aligned}\gamma_b&=-8[L(L+1)-\Lambda^2]B_0^2/h^2\omega^2,\\ \delta_b&=-[L(L+1)-\Lambda^2]\alpha/h\omega\end{aligned}\right\} \tag{26}$$

previously given by Kronig[10] and Dieke,[11] respectively. Here α is defined as in (22). It is to be cautioned that use of (26), even in a first approximation, is allowable only when the molecule is in a paramagnetic state $L\neq 0$ in the united atom approximation. When $L=0$, it is not allowable to disregard Q_{nn}, S_{nn} in comparison with P_{nn}, or overlook the variation of the integral in (12) with r. Even when $L\neq 0$, this procedure is questionable unless we are dealing with highly excited states in which the molecule behaves nearly like the united atom.

(c) L Uncoupling

The remaining isotope corrections (c–d) arise because the separation of variables (9) is not accurate, or in other words because rotation and vibration introduce interactions between different electronic states. These interactions can be divided into two types: (c) Those connecting states whose Λ's differ by one unit and (d) those joining states of equal Λ.

We shall not write down the perturbing terms in the Hamiltonian function which introduce matrix elements between states differing by unity in Λ. Such terms are well known, and give rise to the phenomenon commonly called L uncoupling. They make B^* different from B, and so influence the isotope ratios, as Professor Mulliken first pointed out to me.[12] In the case of a Σ state, calculation shows[13] that

$$\gamma_c=4B_0\textstyle\sum_\Pi|P_y(\Pi\,;\Sigma)|^2/h\nu(\Sigma\,;\Pi), \tag{27}$$

where $$P_y(\Pi\Sigma)=\int\cdots\int\Phi_\Pi{}^\dagger\mathbf{P}_y\Phi_\Sigma d\tau,$$

with $\mathbf{P}_y$ defined as after (13) and where the summation is over all Π levels. In writing (27), we have assumed that in electron bands, the electronic frequencies are not appreciably modified by vibration. With the hypothesis of pure precession explained above near the end of fine print, only one of the Π states gives a perturbation, and (27) reduces to

$$\gamma_c=2B_0L(L+1)/h\nu(\Sigma\,;\Pi). \tag{28}$$

The reader is referred elsewhere[14] for the formulas in the case of Π levels. Here B^* is different for the two components of a Λ doublet. In fact, it is precisely this difference which causes the doubling.

[10] R. de L. Kronig, Physica **1**, 617 (1934).
[11] G. H. Dieke, Phys. Rev. **47**, 661 (1935).

[12] It is hard to say where it was first seriously suggested that L uncoupling modifies the isotope effect. Even before wave mechanics, Mulliken intimated that interaction between electronic motion and vibration might modify isotope behavior (Phys. Rev. **25**, 126 (1925)). The requisite formulas of quantum mechanics were given in reference 4, while later papers by Mulliken repeatedly stressed the distinction between B^* and B, including the case of Σ states (cf. Mulliken and Christy, Phys. Rev. **38**, 92 (1931), Eq. (8)). Very specific applications to the isotope effect have been made by Dieke.[20]

[13] Mulliken and Christy's Eq. (8) has a factor 8 rather than 4 as in our (27) because their convention is to include in the Π summation only one Λ-doublet component in a $\Lambda=1,\ -1$ system of representation. In such a system both components contribute equally, whereas only one component is effective if passage is made to wave functions of the proper final $+-$symmetry.

[14] J. H. Van Vleck, Phys. Rev. **33**, 487 (1929).

L uncoupling is primarily a rotational effect, and so one would expect it not to affect the vibrational isotope ratio. More detailed investigation shows this to indeed be the case, so that one can take

$$\delta_c = 0. \tag{29}$$

(d) Interaction between States of Equal Λ

We have postponed discussion of this interaction until now, as its influence on ω^* has not previously been treated, and requires some study. Let n and n' be two different electronic states of equal Λ whose vibrational quantum numbers are v and v'. The perturbing Hamiltonian matrix element connecting them is[15]

$$H_{nn'}(v\,;v') = \int R^{\dagger}_{nv}[P_{nn'}+Q_{nn'}+S_{nn'} + (-ih/2\pi M)\Omega_{nn'}\mathbf{p}_r]R_{n'v'}d\tau, \tag{30}$$

where $\mathbf{p}_r$ is the operator $h\partial\cdots/2\pi i\partial r$, where $P_{nn'}$, $Q_{nn'}$, $S_{nn'}$ are defined as in (12), (13), (14) and where

$$\Omega_{nn'} = \int \Phi_n{}^{\dagger}(\partial\Phi_{n'}/\partial r)d\tau. \tag{31}$$

The centrifugal term $[J(J+1)-\Lambda^2]h^2/8\pi^2Mr^2$ does not appear in (30), as it makes no contribution because of the orthogonality of Φ_n, $\Phi_{n'}$. Hence the present effect (d) does not influence the rotational isotope behavior, and we can take

$$\gamma_d = 0. \tag{32}$$

On the other hand, it gives a modification in the vibrational case, as we shall show that

$$\delta_d = 2\sum_{n'}\frac{r_0{}^2|\,\Omega^0{}_{nn'}\,|^2B_0}{h\nu(n\,;n')}. \tag{33}$$

Here the summation is over all states of the same Λ as the given state n. When dealing with Σ states, however, only states of the same $+-$ symmetry need be considered, as (30) vanishes if n relates to a Σ^+, and n' to a Σ^- state, or *vice versa*.[16] The zero superscript in (33) means that (31) is to be evaluated at $r=r_0$.

[15] See reference 4 for the mathematical basis underlying the construction of the matrix elements (30). Besides the terms in (30), there are nondiagonal matrix elements due to the cross products between ∇f and $\nabla\Phi_n$ in (15), which no longer necessarily give a vanishing effect when $n\neq n'$. The resulting contribution, however, does not depend appreciably on the vibrational quantum number, but rather primarily on the translational energy of the molecule, and so can be omitted for our purposes.

[16] For what is meant by Σ^+ and Σ^- states, see R. S. Mulliken, Rev. Mod. Phys. **3**, 92 (1931).

It will be noted that (33) involves Ω but not P, Q, S despite the fact that P, Q, S and Ω appear additively in (30). The reason is that the matrix elements due to P, Q, S are smaller than nonvanishing elements due to $(h/2\pi M)\Omega$ by a factor of the order of magnitude $(B_0/h\omega_0)^{\frac{1}{2}}$ as is seen by a simple dimensional examination. Hence we have not bothered to include any of the former in (33), nor shall we in future Eqs. (36), etc. The physical basis of this diversity in size is that $R_{n'v'}$ varies much more rapidly with r than $\Phi_{n'}$ does; i.e., the operator $h\partial\cdots/2\pi i\partial r$ applied to $\Phi_{n'}$ as in (13) is equivalent in order of magnitude to multiplication by $h/2\pi r_0$, whereas when applied to $R_{n'v}$, it is the vibrational momentum operator $\mathbf{p}_r$, which is of the order $(Mh\omega_0)^{\frac{1}{2}}$ by (20). The larger size of the Ω than the other perturbing terms appears to have previously been overlooked, and explains why the Ω terms are able appreciably to modify ω^* despite the fact that they appear only connecting different electronic states, and so enter finally only in formulas involving the electronic frequencies in the denominator. The usual L uncoupling terms, to be sure, are able to modify B^*, but then B^* represents a smaller energy term than ω^*. Fortunately, the Ω terms vanish in the diagonal case $n=n'$, as one can prove that Ω_{nn} equals zero by differentiating (24) with respect to r. The proof applies even when Φ_n is complex, provided one utilizes the structure of Φ_n explained after Eq. (24). Since $\Omega_{nn}=0$, we omitted any mention of the Ω terms in discussing the diagonal effect (b).

Proof of (33). By a common formula of perturbation theory, the shift in energy due to the totality of matrix elements (30) is

$$\Delta W = \Sigma_{n'v'}H_{nn'}(v\,;v')H_{n'n}(v'\,;v)/h\nu(nv\,;n'v'). \tag{34}$$

Usually the denominators of (34) depend but to a small extent on the vibrational quantum number, and may be replaced to a sufficient approximation by expressions $h\nu(n\,;n')$ which can be taken outside the v' summation. Then (34) becomes

$$\Delta W = \Sigma_{n'}\{[\Sigma_{v'}H_{nn'}(v\,;v')H_{n'n}(v'\,;v)]/h\nu(n\,;n')\}. \tag{35}$$

Furthermore

$$\Sigma_{v'}H_{nn'}(v\,;v')H_{n'n}(v'\,;v) = (-hi/2\pi M)^2\int R_{nv}{}^{\dagger}\Omega_{nn'}\mathbf{p}_r\Omega_{n'n}\mathbf{p}_rR_{nv}d\tau. \tag{36}$$

It is clearly to be understood that the summation in (36) does not lead to true matrix multiplication, as the initial and final wave functions in (33) belong to different sets of orthogonal functions because the states n and n' have

different radial constants. Summation over n' in addition to v' would be necessary to give the ordinary case. However, the writer has shown elsewhere that even without summing over n' it is allowable to use formulas such as (36).[17]

The important point is that in (36) we have an expression which does not require knowledge of the vibrational wave functions for the perturbing electronic state n'. To evaluate (36) we expand $\Omega_{nn'}$ (and $\Omega_{n'n}$) as a Taylor's series

$$\Omega_{nn'} = \Omega^0{}_{nn'} + \Omega^{(1)}{}_{nn'}(r-r_0) + \cdots$$

about the equilibrium position for the state n. For our purposes, only the constant term $\Omega^0{}_{nn'}$ is needed, as the remainder would introduce higher powers of $(v+\frac{1}{2})$ or of $B/h\omega_0$. With this approximation, (35) becomes

$$\Delta W = (h^2/4\pi^2M^2)p^2{}_{nn}(v\,;v)\Sigma_{n'}|\,\Omega^0{}_{nn'}\,|^2/h\nu(n\,;n'). \quad (37)$$

Here use has been made of the relation $\Omega_{n'n} = -\Omega^\dagger{}_{nn'}$ obtained by differentiating (24) with respect to r. The diagonal element $p^2{}_{nn}(v\,;v)$ is the same as the mean value of $p_r{}^2$ and so can immediately be obtained from (20). The latter shows that (37) is proportional to $v+\frac{1}{2}$ and so contributes to the ω^* part of (1). Formula (33) for δ_d then follows when one uses the definatory relation (6).

Signs and Relative Magnitudes of the Various Corrections

First we shall consider the subject of sign. Usually the empirical isotope ratios are nearer unity than are the ideal values (4). This behavior is predicted by theory if γ and δ are negative since in all four cases the corrections to (4) become more important the smaller the reduced mass.[18] Now any of the four effects (a–b–c–d) are more apt to give negative than positive contributions to γ or δ and so the observed behavior is quite understandable. The detailed situation on sign for each effect is as follows. In (a), the sign of γ_a or δ_a depends by (7–8) on the a_i in (3) or in other words on the type of anharmonicity or exact shape of the potential curve. In only two cases, *viz.*,[19] the $(2s\sigma)^2\,{}^1\Sigma$ and $2s\sigma 2p\sigma\,{}^1\Sigma$ states of LiH, is this information known with sufficient accuracy to permit the calculation of γ_a, δ_a. In both cases γ_a is negative, also δ_a for $2s\sigma 2p\sigma\,{}^1\Sigma$, but δ_a is positive for $(2s\sigma)^2\,{}^1\Sigma$. The values of γ_b and δ_b are negative if one uses the approximation (26) based on pure precession, since the spectroscopic constant α is usually positive. The same sign behavior will also be found true (cf. Eqs. (43)) when we develop approximations for other limiting conditions. So γ_b and δ_b are probably usually negative. Both δ_c and γ_d vanish, while Eqs. (27) and (33) show that γ_c and δ_d are negative if the dominant frequency denominators are negative (i.e., relate to absorption), which is surely the case if the given state is the ground level of the molecule.

As to the relative importance of the various corrections, it is hard to make a definite prediction. The effect (c) should have a preponderant influence if there is close by a state differing by one unit in Λ. Since $\delta_c=0$, the departures from (4) should then be very much greater in the rotational than in the vibrational isotope effect. Dieke[20] has shown that an interesting example of precisely this situation is provided by the $3p\,{}^3\Sigma$ state of the hydrogen molecule, and that the observed deviation from (4) agrees remarkably well with that calculated from (28), which is here more important than any other correction by a factor ten or so.

Similarly, (d) should be the most important effect if there is a nearby state of the same Λ and same $+-$ symmetry as the level under consideration. Since $\gamma_d=0$, there would then be a much larger correction to the vibrational than to the rotational isotope effect. It would be very gratifying if this point could be tested experimentally.

When there are no nearby states, so that one does not have the resonance cases just cited and instead the frequency denominators are comparable with ionization potentials, it is impossible to say which of the various corrections is the largest without detailed and laborious investigation. The different effects (a–b–c–d) are then of the same rough order of magnitude, as we will later show more fully by some illustrative calculations (except for effect a) on the ground state of the hydrogen molecule. Too much weight should not be attached to the fact that (7), (8), and (17) are proportional to $B_0{}^2/h^2\omega_0{}^2$, and (27) and (33) to $B_0/h\nu$, where ω_0 and ν are respectively vibrational and electronic frequencies. To be sure, $B_0{}^2/h^2\omega_0{}^2$, being quadratic in B_0, is some-

[17] J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 754 (1929).

[18] In all cases (a)–(d), γ and δ involve factors $B_0{}^2/h^2\omega_0{}^2$ or $B_0/h\nu$ and so are apparently inversely proportional to the reduced mass M. However, the terms k_1k_2 in (17), or Ξ, Θ in (38) may involve M_1/M_2. This is shown by (43) or (46–7–8). Even though the mass dependence can thus be more complicated, the dominant factor is usually $1/M$.

[19] F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **49**, 745 (1936).

[20] G. H. Dieke, Phys. Rev. **48**, 606, 610 (1935).

what smaller than $B_0/h\nu$ even when one is well away from resonance. For example, the former is 0.0002 and the latter 0.0006 in the case of the ground state of the hydrogen molecule, a rather extreme example of nonresonance as $\nu = 0.9 \times 10^5$ cm^{-1}. However, the difference in magnitude is not large, and we shall later see (cf. Eqs. (43)) that under certain limiting conditions (17) can be transformed into formulas not involving ω_0 at all. Any disparity resulting from the diversity in size of $B_0^2/h^2\omega_0^2$ and $B_0/h\nu$ can easily be offset by abnormally small or large numerical coefficients in the formulas. In particular the large numbers occurring in (7) and (8) are to be noted as they may make the anharmonic effect (a) fully as important as any of the other corrections except near resonance. However, Crawford and Jorgensen[19] find that in LiH, (a) is able to account for only a fraction of the empirical isotope correction; namely, the empirical values of γ, δ for the $(2s\sigma)^2\,{}^1\Sigma$ state are -0.0005, -0.00019, while the calculated values of γ_a, δ_a are -0.0001, $+0.00008$; for the $2s\sigma 2p\sigma\,{}^1\Sigma$ level, γ, δ are -0.010, -0.027, and γ_a, δ_a give -0.003, -0.004. It is interesting that γ_a/γ has about the same value for both levels despite the fact that one has a γ twenty times as large as the other. The large value -0.027 of δ in the upper state is perhaps indicative of a large effect of type (d). At any rate, the inadequacy of (a) alone seems to corroborate our statement that (a–b–c–d) likely simultaneously can play an appreciable role. When the united atom has an angular momentum, (b) is more important than otherwise (cf. remarks following Eq. (40)).

Digression on Perturbations in Band Spectra

At this point we shall insert a few words on perturbations in general in diatomic spectra, for the underlying mathematical analysis is the same as for the isotope corrections. Dieke[21] has called attention to the fact that perturbations connecting states differing by one unit in Λ increase rapidly with the rotational quantum number J, all other things being equal, and cites confirmatory experimental evidence. Eq. (37) shows that interaction between states of equal Λ increases with the vibrational quantum number v. This fact has not apparently been stressed previously, and it would be very interesting if appropriate experimental evidence could be obtained.[21a] The confirmation would be more difficult than in the preceding case $\Delta\Lambda = \pm 1$, for the dependence on the quantum number is masked if there is much alteration in the frequency denominator, and of course the frequency depends much more on the vibrational than on the rotational quantum number. In other words, in studying perturbations in band spectra, one is apt to be near resonance, and this is just the place where one cannot pass from (34) to (35). Effect (c), L uncoupling, is primarily a rotational phenomenon, whereas (d) is due mainly to vibration, and this distinction explains why one type of perturbation should vary markedly with J and the other with v.

Simplification of the Formulas Under Limiting Conditions

For estimating orders of magnitude, it is convenient to simplify some of the formulas further.

Centroid approximation. If we assume that all the frequency denominators can be regarded as having sensibly the same value $h\nu$, an assumption warranted if at all only when one is well away from resonance, then (27) and (33) become

$$\gamma_c = 2B_0\Xi_0/h\nu, \quad \delta_d = 2B_0 r_0^2\Theta_0/h\nu, \tag{38}$$

where Ξ_0 and Θ_0 denote the integrals defined in (12) and (23), respectively, evaluated for $r = r_0$, $n' = n$. The first formula of (38) follows from (27) by simple matrix multiplication, if ν is constant, inasmuch as $\mathbf{P}_x^2$ and $\mathbf{P}_y^2$ contribute equally to Ξ. The second relation is established from (33) in an analogous fashion by noting that the $\Omega_{nn'}$ are the coefficients in the expansion of $\partial\Phi_{n'}/\partial r$ in terms of the orthogonal functions Φ_n (cf. Eq. (31)).

Behavior of P_{nn}, Q_{nn}, S_{nn} for separated and united atoms. Especially in connection with the specific isotope shift to be considered later, it is illuminating to study the limiting values of P,

[21] G. H. Dieke, Phys. Rev. **47**, 870 (1935).

[21a] *Note added in proof.* Dieke finds that an example is furnished by the $1s\sigma 2s\sigma\,{}^1\Sigma$ state of H_2 (paper presented at Washington meeting of Am. Phys. Soc., 1936).

Q, S, defined in (12)–(13)–(14) when the nuclei 1, 2 are infinitely far apart or coalesced together. The results are as follows

$$r=\infty\begin{cases}P_{nn}\text{ or }2Q_{nn}\rightarrow\frac{2}{3}(M_1w_2+M_2w_1)/M_{1+2},\\ S_{nn}\rightarrow(M_1w_1+M_2w_2)/M_{1+2},\end{cases}\tag{39}$$

$$r=0\begin{cases}P_{nn}\text{ or }2Q_{nn}\rightarrow\frac{2}{3}(M_1Z_2-M_2Z_1)^2w_{1+2}/M_1M_2Z^2{}_{1+2},\\ S_{nn}\rightarrow w_{1+2}.\end{cases}\tag{40}$$

Here w_1, w_2 denote the energy corrections for the motion of the nucleus for isolated atoms 1, 2, respectively, and w_{1+2} that for the united atom. Z_1 and Z_2 are the nuclear charges of atoms 1 and 2. Eq. (39) applies only if the dissociation products are atoms in S states, as the proof assumes that the kinetic energy, etc., is prorated equally between the x, y, and z directions. If this condition is not fulfilled, the sum $P_{nn}+Q_{nn}$ is still given correctly by (39). Similarly, if the united atom has an angular momentum, (40) should be used only to obtain the sum $P_{nn}+Q_{nn}$, and furthermore in this case there is the extra term $[L^2+L-\Lambda^2]/8\pi^2Mr^2$ not included in (40) (cf. Eq. (26)). Its inclusion means that P_{nn} becomes infinite when $r\rightarrow 0$ if $L\neq 0$. This apparently absurd result is obtained because the perturbation calculations all assume that the electronic charge cloud rotates with the nuclei; actually the two will become decoupled when r is made too small. However, for actual values of r, the decoupling has usually only started, and the large values in the limit $r=0$ explain why $P_{nn}(r)$, and hence effects (b)–(c), are abnormally important when the united atom has an angular momentum. It is usually assumed that in (12) the integral Ξ_{nn} does not vary much with r, but (39) shows that for large values of r, the factor Ξ_{nn} is proportional to r^2 inasmuch as $P_{nn}=\Xi_{nn}h^2/8\pi^2Mr^2$ is independent of r when $r\rightarrow\infty$.

A sketch of the arguments used to obtain (39)–(40) is as follows: The values of S_{nn} for $r=\infty$ and $r=0$ are quite obvious, as for $r=0$ S_{nn} is simply the usual correction term for nuclear motion,[22] while for $r=\infty$ it would be except that it has a mass factor $1/M_{1+2}$ rather than $1/M_1$ or $1/M_2$. The behavior of $P_{nn}+Q_{nn}$ at $r=\infty$ is obtained by noting that when r is varied with the center of gravity held fast, the origin of atom 1 is displaced by an amount M_2/M_{1+2} and that of atom 2 by M_1/M_{1+2}. Furthermore the P_{nn} and Q_{nn} terms then combine to involve essentially the Laplacian operator $\nabla^2{}_{XYZ}$, as far as each nucleus is concerned, except for a numerical factor $-(h^2/8\pi^2)(M_2{}^2/MM^2{}_{1+2})$ or $-(h^2/8\pi^2)(M_1{}^2/MM^2{}_{1+2})$. Here M is the reduced mass M_1M_2/M_{1+2}. As already stated, the apportionment between P_{nn} and Q_{nn} given in (39) is correct only if the isolated atoms are isotropic. The behavior of $P_{nn}+Q_{nn}$ at $r=0$ follows on observing that if the nuclei are drawn infinitesimally far apart with their center of gravity preserved at the origin, the change in the potential field may be regarded as equivalent to that of a dipole, and the dipole is $(Z_1M_2-Z_2M_1)/M_{1+2}Z_{1+2}$ times as intense as for the purely translational or S effect. This accounts for a factor $(Z_1M_2-Z_2M_1)^2/M^2{}_{1+2}Z^2{}_{1+2}$ in the behavior of $P_{nn}+Q_{nn}$ as compared with S_{nn}; the remaining factor $M^2{}_{1+2}/M_1M_2$ is because of the different mass denominators in (12–13) and (14). It may seem strange that P_{nn} does not vanish at $r=0$ when $L=0$; the reason for this paradox is that the center of gravity does not coincide with the nuclear midpoint, so that the angular momentum about the former need not vanish even though that about the latter does.

If one neglects the cross terms $j\neq i$ in (14), the expression w_1 equals m/M_1 times the kinetic energy of atom 1. With a similar approximation, w_{1+2} is m/M_{1+2} times the kinetic energy of the united atom, where m is the mass of one electron. Actually, nonvanishing cross terms owe their existence to the fact that the complete wave function is not expressible as the product of wave functions of individual electrons, either because of antisymmetrization, or because the interelectronic distances enter explicitly as arguments. The calculations of Hylleraas[22] show that the cross terms resulting from the latter cause, are unimportant, at least in the ground state of helium. The work of Hughes and Eckart[23] indicates that in atoms the antisymmetrization affects the nuclear corrections appreciably only if at least one electron is in a p state. In molecules, it will give an appreciable contribution at medium internuclear distances even when electrons are only in s states, due to the overlap of wave functions of the different atoms. However, at any internuclear distance, we can neglect the cross terms if we are interested only in orders of magnitudes, and so a very simple rough formula for S_{nn} is

$$S_{nn}=(m/M_{1+2})T,\tag{41}$$

where T is the total kinetic energy of the electrons. The virial theorem[24] tells us that

$$T=-E_n-r\partial E_n/\partial r,\tag{42}$$

[22] Cf. E. A. Hylleraas, Zeits. f. Physik **54**, 364 (1929).

[23] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

[24] Cf. J. C. Slater, J. Chem. Phys. **1**, 687 (1933); W. Pauli, Ann. d. Physik **68**, 177 (1922).

and so if (41) is accepted, the variation of S with r, as required for (16), can immediately determine if we know the potential energy curve $E_n(r)$, as in (3). In (42) the origin for the energy E_n must be so chosen that E_n vanishes when the molecule is blown completely to pieces (individual isolated charges). Eqs. (40) show that in symmetrical molecules the P and Q terms are negligible compared with S at small internuclear distances, provided $L=0$, and so for estimating orders of magnitude, it is natural to neglect P, Q in comparison with S, and use (41–42) and (3). Then (17) becomes

$$\gamma_b=-2m/M_{1+2}. \quad \delta_b=-3m/2M_{1+2}. \tag{43}$$

Calculation of P_{nn}, Q_{nn}, S_{nn} for Wang Hydrogen Functions

The values of P_{nn}, Q_{nn}, S_{nn} can be computed for any value of r for the normal state of the hydrogen molecule if one use the well-known Wang[25] wave functions

$$\Phi_n=A(e^{-b(r_{1a}+r_{2b})}+e^{-b(r_{1b}+r_{2a})}). \tag{44}$$

Here r_{1a} is the distance of electron a from nucleus 1, etc., and the normalization constant A has the value

$$1/A^2=(2\pi^2/b^6)[1+e^{-2br}(\tfrac{1}{3}b^2r^2+br+1)^2]. \tag{45}$$

By simple integrations, most easily made in elliptic coordinates, one finds that

$$P_{nn}=B_0(4\pi^2r_0^2A^2/18b^4)[3-e^{-2br}(b^2r^2+3br+3)(br+1)]+[(M_1-M_2)/2M_{1+2}]^2B_0g, \tag{46}$$

$$Q_{nn}=-B_0(r_0\partial \log A/\partial r)^2+[2(M_2^2+M_1^2)/M^2{}_{1+2}]\alpha B_0-4(M_1M_2/M^2{}_{1+2})\beta B_0, \tag{47}$$

$$S_{nn}=B_0g(M_1M_2/M^2{}_{1+2})+4(M_1M_2/M^2{}_{1+2})(\alpha+\beta)B_0, \tag{48}$$

with

$$g=(8\pi^2r_0^2A^2/3b^4)[1+e^{-2br}(br+1)(\tfrac{1}{3}b^2r^2+br+1)], \tag{49}$$

$$\alpha=(\pi^2r_0^2A^2/3b^4)[1+\tfrac{1}{3}(br+b^2r^2)^2e^{-2br}], \tag{50}$$

$$\beta=(\pi^2b^2r_0^2A^2/3b^4)(-b^2r^2+br+1)(1+br+\tfrac{1}{3}b^2r^2)e^{-2br}. \tag{51}$$

These formulas conform to (39–40) in the limiting cases.[26]

Estimate of the Various Terms for the Ground State of the Hydrogen Molecule

The shape of the potential curve is not known with sufficient precision for the ground level of hydrogen so that γ_a, δ_a can be evaluated. However, the preceding calculations enable us to determine roughly the corrections due to the other causes (b–c–d). We shall let primes refer to H_2, double primes to HD, and triple primes to D_2. When Wang's optimum value $1.166/a_0$ is substituted for the screening constant b at the actual internuclear distance $r=1.406a_0(a_0=h^2/4\pi^2e^2m)$, (46) and (47) give

$$\Xi_0'=\Xi_0'''=0.394, \quad \Xi_0''=0.486, \quad \Theta_0'=\Theta_0'''=0.335/r_0^2, \quad \Theta_0''=0.377/r_0^2. \tag{52}$$

For the centroid frequency ν, following Frank and V. V.,[27] we shall use the value $1.23R$, where R is the Rydberg constant. Then (38) yields

$$\begin{aligned}&\gamma_c'=-0.00035, \quad \gamma_c''=-0.00032, \quad \gamma_c'''=-0.00017,\\ &\delta_d'=-0.00030, \quad \delta_d''=-0.00025, \quad \delta_d'''=-0.00015,\end{aligned} \tag{53}$$

while from (43) we have

$$\begin{aligned}&\gamma_b'=-0.00054, \quad \gamma_b''=-0.00036, \quad \gamma_b'''=-0.00027,\\ &\delta_b'=-0.00041, \quad \delta_b''=-0.00027, \quad \delta_b'''=-0.00020.\end{aligned} \tag{54}$$

[25] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[26] The values of w_i and w_{1+2} yielded by the Wang functions are, respectively, $h^2b^2/8\pi^2M_i$ and $2b^2h^2/8\pi^2M_{1+2}$.

[27] A. Frank and J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 539 (1929). This paper gives details of the calculation of Ξ_0 for H_2.

Eqs. (54) should be regarded as probably giving only upper limits to the absolute values of γ_b and δ_b, as (43) assumes that $P_{nn}+Q_{nn}$ can be neglected in comparison with S_{nn}. Since the w's are positive, Eqs. (39–40) show that $P_{nn}+Q_{nn}$ is larger for $r=\infty$ than for $r=0$ whereas the reverse is true of S_{nn}. Hence $\partial(P_{nn}+Q_{nn})/\partial r$ is doubtless opposite in sign to $\partial S_{nn}/\partial r$. So $P_{nn}+Q_{nn}$ gives a contribution to k_1 in an opposite direction to that from S_{nn} (cf. Eq. (16)) and so by (17) tends to offset the S_{nn} effect in γ_b and in at least part of δ_b. Of course one can reckon γ_b, δ_b without disregarding $P_{nn}+Q_{nn}$ in comparison with S_{nn}, by expanding (46)–(47)–(48) about the equilibrium position. If one neglects the variation of b with r, then one obtains a value 0.0004 for γ_b which is of the opposite sign from that given in (54). In all likelihood γ_b is actually negative since (39)–(40) show that $P_{nn}+Q_{nn}+S_{nn}$ is greater for $r=0$ than for $r=\infty$,[28] making $\partial(P_{nn}+Q_{nn}+S_{nn})/\partial r$ presumably negative. On the other hand (46)–(47)–(48) yield a smaller value of $P_{nn}+Q_{nn}+S_{nn}$ for $r=0$ than for $r=\infty$ if the same value of b is used in both limits. This fact makes it clear why expansion of (46)–(47)–(48) gives a γ_b of the wrong sign if b is treated as constant. A more refined calculation, in which b varies with r, does not seem repaying at the present time. Even the leading term k_0B_0 in (16) as obtained from (46)–(47)-(48) involves some error because b was regarded as independent of r in computing the integral Θ_{nn} in (23). However, the error is probably not as serious as in the higher r derivatives involved in connection with k_1, k_2 in (16), and Wang's success in computing ω_3 without letting b depend on r is indicative that the variation of b with r is not too important in lower derivatives.

Unfortunately, no adequate experimental data on the ground state of the hydrogen molecule are available to test (53)–(54). For excited states, Dieke[11] calculates from (26) isotope corrections not a great deal larger than (53)–(54), being still of the order of magnitude $\gamma'-\gamma''\sim 10^{-4}$. The effect (26) considered by him is present only when the united atom has a nonvanishing angular momentum L. The ground state of the hydrogen molecule has $L=0$, and our main purpose in presenting (53)–(54) is to show that even without the anharmonic effect (a), not all of the isotope correction is connected with the existence of an $L\neq 0$.

The Electronic Isotope Shift

The difference in the constant terms in the energy for two isotopes is usually called the electronic isotope shift. It consists mainly in the difference in the constant part k_0B_0 of (16), or in other words in $P_{nn}+Q_{nn}+S_{nn}$ evaluated at $r=r_0$, for the two isotopes. Dieke has had some success in explaining approximately the observed isotope shifts by neglecting Q_{nn}, S_{nn} in comparison with P_{nn}, and assuming for the latter the value

$$P_{nn}=B_0[L(L+1)-\Lambda^2] \tag{55}$$

furnished by the hypothesis of pure precession. A somewhat better approximation is probably to add to (55) the value of S_{nn} furnished by (41)–(42). As noted by Dunham[2] and Dieke,[11] the anharmonic correction (a) also makes a contribution

$$Y_{00}=(B_0/8)(3a_2-7a_1^2/4) \tag{56}$$

to the constant part of the energy. In the cases studied by Dieke,[11] the effect of (56) is unimportant. The inclusion of S_{nr}, however, alters the calculated values somewhat, as shown in the following table. Our various formulas, though ostensibly for singlets, can be applied to triplets in hydrogen since here the multiplet width is negligible.

	H_2-HD Calculated		Obs.	$HD-D_2$ Calculated		Obs.
	(55)-(56)	(41)-(55)-(56)		(55)-(56)	(41)-(55)-(56)	
$3p\,^3\Pi-2s\,^3\Sigma$	7.60	6.07 cm^{-1}	5.01	7.66	6.89 cm^{-1}	4.94
$3p\,^3\Sigma-2s\,^3\Sigma$	13.00	11.92	13.23	12.17	11.64	12.28

Clearly it is not allowable to neglect $Q_{nr}+S_{nn}$ in comparison with P_{nn} unless at least either the initial or final state has $L=0$. Even when this condition is met, it is no longer allowable to overlook $Q_{nn}+S_{nn}$ if the line is in the ultraviolet. By (41), the S_{nn} effect is more important the shorter the wave-length, as then there is more difference, and hence less cancelation, between the values of (41) for the initial and final states. Examples are the lines, all in the ultraviolet, terminating on the ground state of the hydrogen molecule. To make an approximate calculation, we can use (46)–(47)–(48)

[28] If one neglects the cross terms in (14), then use of observed energies and the virial theorem shows that the actual values of w_1 and w_{1+2} for H and $^2He_2$ are, respectively, $R/1840$ and $5.8R/3680$, where R is the Rydberg constant.

for the ground state, and assume that in the upper state, the effect of the inner electron can be computed by using the Finkelstein-Horowitz[29] wave function $C(e^{-dr_{1a}}+e^{-dr_{2a}})$ for H_2^+. The latter yields

$$P_{nn}+Q_{nn}+S_{nn}=B_0[(C^2\pi r_0^2/d)-(r_0\partial \log C/\partial r)^2] \tag{57}$$

with $d^3/2\pi C^2=1+e^{-dr}(\frac{1}{3}d^2r^2+dr+1)$. The optimum value of dr is 2.46. From (46)–(47)–(48) one finds

Ground state	H_2	HD	D_2
$P_{nn}+Q_{nn}+S_{nn}$	114	85	57 cm^{-1}

The corresponding values for H_2^+, HD^+, D_2^+ furnished by (57) are, respectively, 59, 44, 29 cm^{-1}. In the case of H_2, the apportionment of 114 between P_{nn}, Q_{nn}, and S_{nn} is, respectively, 23, 20, and 71 cm^{-1}; Eq. (41) would give 69 cm^{-1} for S_{nn}. (In HD, the apportionment between P_{nn}, Q_{nn}, S_{nn} is different, but the total effect is inversely proportional to the reduced mass M, as one sees by adding (46), (47), (48).) To obtain the total shift, one must add the anharmonic correction obtained from (56), and, in the upper state, the effect of the outer electron as given by (55). The corresponding isotope shifts for H_2-HD are shown in the following table. It is seen that the largest contribution comes from (46)–(47)–(48)–(57), i.e., from the S_{nn} terms, while (55) alone does not even give the right sign

H_2-HD Calculated	Eq. (55)	(56)	(46)–(47)–(48)–(57)	Total	H_2-HD Obs.	$\frac{1}{2}(H_2-D_2)$ Obs.
$2p\ ^1\Pi-1s\ ^1\Sigma$	+7.4	−2.7	−13.8	−9.1	−8 cm^{-1}	−12 cm^{-1}
$2p\ ^1\Sigma-1s\ ^1\Sigma$	+9.7	−0.8	−13.8	−4.9	−12	− 2

The discrepancies here may be due to the very considerable experimental error, estimated by Dieke as 5 to 10 cm^{-1}, and to the inaccuracies of the Wang and Finkelstein-Horowitz wave functions.[30] The $2p\ ^1\Sigma$ state has an equilibrium distance 1.31×10^{-8} cm whereas $2p\ ^1\Pi$ has almost exactly that 1.06×10^{-8} of H_2^+. Our H_2^+ treatment of the inner electron should thus apply better to $2p\ ^1\Pi$, and possibly this circumstance explains the greater disagreement for the transition involving $2^1p\ ^1\Sigma$. At any rate, the observed shifts are qualitatively understandable. In the table we have also included half the observed displacement between H_2 and D_2. This should equal the H_2-HD shift according to our formulas, and doubtless more generally. The discrepancy between the measured value for H_2-HD and half that for H_2-D_2 is hence indicative of a considerable experimental error.

The Mean Square Angular Momentum of the Normal H_2 Molecule

In connection with the diamagnetism of H_2, as well as with the determination of nuclear spin by means of Stern-Gerlach experiments on the hydrogen molecule, it is necessary to evaluate the integral Ξ_{nn} defined in (12). Miss Frank and the writer obtained 0.394 with the Wang wave functions (cf. Eq. (52)). Wick[31] obtained $\Xi_{nn}=0.02$ with other wave functions $De^{-(r_{1a}+r_{2a}+r_{1b}+r_{2b})}$, and suggested that our value was only an upper limit. Eq. (39) makes it clear why Wick obtained such a low result. The type of wave function which he used makes P_{nn} vanish at $r=\infty$, whereas the Wang wave function gives the correct limit. Hence we do not believe that our value is necessarily much, if any too high. It is well below the asymptotic value $\frac{1}{3}b^2r_0^2$ characteristic of large r, which yields $\Xi_{nn}=0.9$ at the actual internuclear distance.

In adapting calculations on the Stern-Gerlach effect to HD rather than H_2, allowance must be made not merely for the altered reduced mass, but also for the somewhat different value of Ξ_{nn} (cf. Eq. (52)), which arises because the center of gravity no longer coincides with the nuclear midpoint. In calculations on diamagnetism, however, it is not necessary to consider this distinction, as the formula for the susceptibility is invariant of the origin.

The writer is indebted to Professors F. H. Crawford and R. S. Mulliken for valuable discussions.

[29] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

[30] In applying (56), we use the values of a_1, a_2 corresponding to the values of α, x given in Miss Sponer's tables. Uncertainty in these constants may be a subsidiary source of error. The experimental value for the H_2-HD shift used in the table is by Jeppesen, as revised by Dieke;[11] that for H_2-D_2 is furnished by very recent work of Jeppesen (paper at Washington meeting, 1936).

[31] G. C. Wick, Zeits. f. Physik **85**, 25 (1933).

Viscosity and Diffusion Coefficients of Atomic Hydrogen and Atomic Deuterium*

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The viscosity of atomic hydrogen has been recalculated from Harteck's experimental values for the relative viscosity of atomic-molecular hydrogen mixtures, on the assumption that atomic hydrogen like molecular hydrogen may be regarded as a van der Waals gas. The numerical results confirm this assumption and permit the evaluation of diffusion coefficients for $H-H_2$, $D-D_2$, $H-D_2$, $D-H_2$ and D–H binary mixtures as well as the viscosity of atomic deuterium.

IN reaction kinetics investigations involving atomic hydrogen, it is often necessary to know the value of D_{12}, the diffusion coefficient of atomic-molecular hydrogen mixtures, in order to estimate the extent of a wall reaction (determined by the rate at which atoms diffuse to the wall). In dynamic systems, the rate at which atoms disappear by diffusion from a given volume element must be considered as well as the rate at which atoms are being removed by pumping. A knowledge of the value of D_{12} is required for such calculations.

It is the purpose of the present communication to reevaluate the existing data for the viscosity of atomic-molecular hydrogen mixtures in order to obtain the value of η_1, the viscosity of atomic hydrogen, from which D_{12} may be calculated.

Harteck[1] has determined the viscosities of atomic-molecular hydrogen mixtures of known composition by applying Poiseuille's equation to the flow of such mixtures through a small tube. His measurements, in which molecular hydrogen was used as the reference gas, yielded relative values, η_{mix}/η_2, at $-80°$, $0°$ and $100°$C. In calculating the relative viscosity of atomic hydrogen, η_1/η_2, from his experimental results Harteck used a formula derived by Puluj[2] which gives the relative viscosity of one component of a binary mixture in terms of the relative viscosities of the other component and of the mixture, and the composition. From the relative values, η_1/η_2, obtained in this way, Harteck attempted to evaluate η_1 at the three temperatures from the known temperature variation of η_2. If the viscosity of atomic hydrogen varies with temperature according to the Sutherland[3] formula we have the relation

$$\eta_{1_T}=\eta_{1_0}\frac{1+(C/273.16)(T/273.16)^{\frac{1}{2}}}{1+C/T}=\Phi(T/273.16)^{\frac{1}{2}}, \quad (1)$$

where η_{1_T} is the viscosity of atomic hydrogen at the absolute temperature T and η_{1_0} that at 0°C (273.16°A). C is the Sutherland constant for atomic hydrogen. Harteck found that at the three temperatures Φ had the same value within his experimental error and concluded that the value of C was extremely small. He appears, however, to have forgotten the $(T/273.16)^{\frac{1}{2}}$ factor since he gives for the value of η_1 at 0°C the mean of the three Φ values. One gets the impression from this that the viscosity of atomic hydrogen does not vary with temperature whereas inclusion of the $(T/273.16)^{\frac{1}{2}}$ factor shows that η_1 actually does increase with temperature.

It has been considered advisable to recalculate Harteck's results since, in addition to the error indicated above, Puluj's formula does not give results which are in agreement with experiment.

In the present calculation it will be assumed that both atomic and molecular hydrogen are van der Waals gases (gases whose molecules are hard elastic spheres of invariable diameter with attractive forces varying as an inverse power of the distance). This is equivalent to the assumption that the viscosities of these gases can be represented by the Sutherland formula. For molecular hydrogen this is actually the case at the temperatures under consideration. Formulas for the viscosities of the mixtures and of the pure gases considered in these calculations will be consistent with the above assumption. In addi-

* Contribution from the Research Laboratory of Physical Chemistry Massachusetts Institute of Technology, No. 367.

[1] P. Harteck, Zeits. f. physik. Chemie **139**, 98 (1928).

[2] J. Puluj, Wien. Ber. **79**, 97, 745 (1879).

[3] W. Sutherland, Phil. Mag. **36**, 507 (1893).

tion, the recombination of atomic hydrogen to molecular hydrogen need not be considered since the rate of recombination is negligibly slow compared to the rate of momentum transfer which determines the viscosity.

Chapman[4] has obtained an expression for the viscosity of a binary gas mixture which, expressed in its general form, is independent of the laws of force governing the attraction and repulsion of the molecules. The derivations of Chapman have been subject to corrections by Enskog[5] giving the expression[6]

$$\eta_{\text{mix}}=\frac{Ax^2+B2x(1-x)+C(1-x)^2}{Ax^2/\eta_1+D2x(1-x)+(C/\eta_2)(1-x)^2}, \quad (2)$$

in which

x = mole fraction of component 1 (atomic hydrogen),

$1-x$ = mole fraction of component 2 (molecular hydrogen),

$$A=1+kM_1/M_2, \quad (3)$$

$$C=1+kM_2/M_1, \quad (4)$$

$$B=(1-k)+\frac{1}{2G}\left(\frac{1}{\eta_1}+\frac{1}{\eta_2}\right), \quad (5)$$

$$D=\frac{(M_1+M_2)^2kG}{2M_1M_2}+\frac{1}{2G\eta_1\eta_2}, \quad (6)$$

where

$$\frac{1}{G}=\frac{(M_1+M_2)}{2}\frac{PD_{12}}{RT}. \quad (7)$$

D_{12} is the diffusion coefficient (at the pressure P) for the mixture, R, the gas constant, M_1 and M_2, the molecular weights of the respective components.

For elastic spheres with an attractive field (van der Waals molecules)

$$k=0.600\frac{1+2C_{12}/3T}{1+C_{12}/T}, \quad (8)$$

where C_{12}, the Sutherland constant for the mixture, is given by[5a]

$$C_{12}=\frac{\gamma(C_1C_2)^{\frac{1}{2}}}{[\frac{1}{2}((d_1/d_2)^{\frac{1}{2}}+(d_2/d_1)^{\frac{1}{2}})]^{\nu-1}}; \quad (9)$$

ν is the exponent in the expression for the attractive force, $F=a/r^\nu$, and γ a constant which is a function of ν having the following values:

ν	3	4	5	7	9
γ	1.140	1.073	1.028	0.968	0.929.

C_1 and C_2 are the Sutherland constants for the pure gases and d_1 and d_2, the respective molecular diameters. In order to use the above expressions in actual calculations it is necessary to know the value of D_{12}. As a first approximation Enskog[5a] gives a formula in which it is considered as being independent of the composition of the mixture. Actually the value changes slightly with composition. If we let the approximate value be D_0, then

$$D_{12}=D_0f(x)=D_0f'(\alpha),$$

where α is the degree of dissociation of molecular hydrogen into atoms, in which case $x=2\alpha/(1+\alpha)$ and $1-x=(1-\alpha)/(1+\alpha)$. The actual dependence of D_{12} upon composition is quite small. Enskog[5a] has evaluated $f(x)$ for the case of elastic spheres without attractive forces and finds that the calculated dependence is confirmed by experiments on real gas mixtures indicating that $f(x)$ is not appreciably different for a gas of van der Waals molecules than for a gas of elastic spheres without attractive forces. According to Enskog, when $(1-x)/x=0(\alpha=1)$

$$D_{12}=D_0\left(1+\frac{M_1^2}{2(6M_1^2+8M_1M_2+15M_2^2)}\right)$$
$$=1.0061D_0$$

and when $x/(1-x)=0(\alpha=0)$

$$D_{12}=D_0\left(1+\frac{M_2^2}{2(15M_1^2+8M_1M_2+6M_2^2)}\right)$$
$$=1.0364D_0.$$

Thus, the value of D_{12} changes by only three percent over the entire composition range. In view of this small variation it will be sufficiently accurate for the present purpose to let

$$f'(\alpha)=a+b\alpha,$$

where a and b, evaluated from the fact that $f'(\alpha)=1.0016$ for $\alpha=1$ and 1.0364 for $\alpha=0$, are equal to 1.0364 and -0.0303. Using Enskog's expression for D_0 for a van der Waals gas

[4] S. Chapman, Phil. Trans. Roy. Soc. **A211**, 433 (1912); **A216**, 279 (1915); **A217**, 115 (1917).
[5] D. Enskog, (a) Inaug. Diss. Uppsala, 1917; (b) Arkiv. for Mat., Astron. och Fysik **16**, No. 16 (1921).
[6] M. Trautz, Ann. d. Physik (5) **18**, 816 (1933).

mixture we obtain finally

$$D_{12}=\frac{3R^{\frac{1}{2}}T^{\frac{1}{2}}}{8(2\pi)^{\frac{1}{2}}N((d_1+d_2)/2)^2(1+C_{12}/T)} \times\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{\frac{1}{2}}\frac{1}{P}(1.0364-0.0303\alpha), \quad (10)$$

where N is Avogadro's number. Upon substituting the value of D_{12} from Eq. (10) into Eq. (7) we obtain

$$\frac{1}{G}=\frac{3(M_1+M_2)^{\frac{1}{2}}R^{\frac{1}{2}}T^{\frac{1}{2}}(1.0364-0.0303\alpha)}{16(2\pi)^{\frac{1}{2}}(M_1M_2)^{\frac{1}{2}}N\left(\frac{d_1+d_2}{2}\right)^2\left(1+\frac{C_{12}}{T}\right)}. \quad (11)$$

To evaluate $1/G$ it is necessary to know the values of d_1 and d_2. The quantity d_2 may be computed directly from measured values of η_2. In order to determine d_1 we shall assume *as a first approximation* that we are dealing with elastic spheres without attractive forces and solve for η_1 (using Harteck's measured values of η_{mix}/η_2). For this calculation it is possible to use rigorous expressions (analogous to Eq. (2)) derived by Enskog.[5a] In such expressions C_{12} obviously does not appear so that by a series of successive approximations it is possible to calculate consistent values of η_1 and d_1. In this manner it is found that at 0°C, $d_2=2.71\times10^{-8}$ cm and $d_1=2.49\times10^{-8}$ cm. The value of η_2 in this calculation is given by the relation

$$\eta_2=\frac{5.882\times10^{-6}T^{\frac{1}{2}}}{1+35.8/T}, \quad (12)$$

obtained by F. G. Keyes (unpublished data) by applying the method of least squares to the existing viscosity data for hydrogen. Eq. (12), however, is the form assumed by the viscosity expression for *attracting* elastic spheres. The rigorous expression given by Enskog[5a] is

$$\eta=\frac{5\times1.016}{16}\left(\frac{RTM}{\pi}\right)^{\frac{1}{2}}\frac{1}{Nd^2(1+C/T)}. \quad (13)$$

As a second approximation in determining d_1 we may determine d_2 from Eq. (13) (in this case, the diameter does not change with temperature), and assume that the *ratio* d_1/d_2 is the same for attracting elastic spheres as for nonattracting elastic spheres. This assumption is equivalent to the assumption that the Sutherland constant for atomic hydrogen is essentially the same as that for molecular hydrogen. We may check our approximate value of d_1 (as well as C_1) when we have finally calculated η_1 from Eq. (2), by means of Eq. (13). This almost amounts to an independent check since Eq. (2) defines the composition dependence and Eq. (13) the temperature dependence of the viscosity coefficient.

In Keyes' expression for η_2, the Sutherland constant, 35.8 is much smaller than the values found in the literature which vary from 70 to 83. There are two reasons for preferring 35.8 as the correct value. First, this value was obtained by the method of least squares applied to over 50 viscosity values in the temperature range $-200°$ to $+300°$C, whereas the high values in the literature are calculated from a small number of viscosity values over a narrow temperature range. Second, the relation between the Sutherland constant and equation of state data clearly indicates that the small value is more reasonable.

We may write the equation of state for a van der Waals gas at not too great pressure in the form[7]

$$P(V-B_0)=RT,$$

where B_0 is given by the expression

$$B_0=-2\pi N\int_0^\infty(e^{-\mathrm{Pot}/kT}-1)r^2dr. \quad (14)$$

In evaluating the integral it must be remembered that under the assumption of a van der Waals gas the intramolecular potential energy "Pot" becomes infinite on contact of two molecules making the integrand zero for all values of r from 0 to d, the diameter of a single molecule. A series integration of Eq. (14) gives the result

$$B_0=\frac{2}{3}\pi Nd^3-\frac{2\pi aN}{18d^3kT}+\cdots \quad (15)$$

if the potential energy is represented by $-a/6r^6$ in accordance with an attractive force a/r^7. Since

$$B_0=\beta-A/RT \quad (16)$$

we have the relations

[7] F. G. Keyes, Chem. Rev. **6**, 175 (1929); F. G. Keyes, L. B. Smith and H. T. Gerry, Proc. Am. Acad. **70**, 319 (1936).

TABLE I.

T(°A)	η_{mix}/η_2	α	$\eta_2\times10^6$	$1/G\times10^6$	k	A	B	C	D	$\eta_1\times10^6$
193.16	0.966	0.650	69.0	84.4	0.572	1.286	$1.040+42.2\times10^{-6}/\eta_1$	2.144	$1.525\times10^4+0.612/\eta_1$	65.3
273.16	0.883	0.637	86.0	104.8	0.579	1.290	$1.030+52.4\times10^{-6}/\eta_1$	2.158	$1.243\times10^4+0.609/\eta_1$	69.4
373.16	0.886	0.591	103.7	126.1	0.584	1.292	$1.024+63.0\times10^{-6}/\eta_1$	2.168	$1.042\times10^4+0.608/\eta_1$	83.2

$$\beta=\frac{2}{3}\pi Nd^3, \quad A=\frac{1}{9}\frac{\pi aN^2}{d^3},$$

where higher series terms in Eqs. (15) and (16) have been neglected. To evaluate C in terms of β and A we make use of the relation derived by Enskog[5a]

$$C=\frac{2\delta Na}{3(\nu-1)d^{\nu-1}R},$$

where, for the present case of $\nu=7(F=a/r^7)$, $\delta=\frac{1}{2}\times0.5165$, so that

$$C=0.5165Na/3\times6Rd^6=2.1\times10^{-9}A/\beta. \quad (17)$$

For hydrogen the values of A and β are 0.2001×10^{12} ergs×cc per mole and 20.96 cc per mole, respectively,[8] so that C calculated from Eq. (17) has the value 20.0.

From Eq. (12) we find that $\eta_2=86.0\times10^{-6}$ poises at 273.16°A, so that d_2 calculated from Eq. (13) is 2.55×10^{-8} cm. The assumed value for d_1, therefore, is $(2.55\times2.49/2.71)\times10^{-8}$ cm or 2.34×10^{-8} cm. In order to evaluate C_{12} from Eq. (9) C_1 is determined from the relation indicated by Keyes,[9] namely, that for nonpolar gases

$$C=KP_0,$$

where P_0 is the molecular polarization and K, a constant which is independent of the gas. For molecular hydrogen $P_0=2.00$[10] while for atomic hydrogen the calculated value is 1.68[11] so that

$$C_1=35.8\times1.68/2.00=30.1.$$

Substituting the proper values in Eq. (9) we find that $C_{12}=31.6$. We are now in position to calculate η_1 from Eq. (2). Table I contains the results of this calculation as well as the values of the constants calculated from Eqs. (3), (4), (5), (6), (8) and (11). The values of η_{mix}/η_2 and α are taken from Harteck's paper.[1]

It is now possible to use the calculated values of η_1 to determine C_1 and d_1 from Eq. (13) as a check upon the values assumed for use in Eq. (2). For this purpose only the η_1 values at 273.16° and 373.16°A will be used, since the value at 193.16°A may be in considerable error as pointed out by Harteck.[1] At this temperature, the capillary used in the experiments became coated with a sheath of ice because of the fact that the atomic-molecular hydrogen mixture contained water vapor to poison the walls against recombination. In addition, Harteck states that at this low temperature the enhanced recombination prevented the gas mixture from assuming the temperature of the surrounding bath (−80°C). Both effects would tend to make η_{mix}/η_2 (and consequently, η_1) too high, in agreement with the high experimental value, 0.966. It is estimated that this value may be in error by as much as ten percent. Solving Eq. (13) simultaneously for C_1 and d_1 by substitution of the last two η_1 values of Table I, we find that $C_1=28.2$ and $d_1=2.42\times10^{-8}$ cm, in good agreement with the provisionally assumed values 30.1 and 2.34×10^{-8} cm. It is now possible to make a second calculation of η_1 values from Eq. (2), using the values of C_1 and d_1 obtained as a result of the first calculation. These approximations may be repeated until subsequent variations in C_1 and d_1 produce changes of less than one percent in the values of η_1. This accuracy is at least as great as that of the experimental η_{mix}/η_2 values at 273.16° and 373.16°A. Table II summarizes the results of a series of such successive approximations, where approximation I is the calculation represented by Table I. Further approximations result in η_1 values that vary within the limits of the last three above approximations; accordingly, we may take as our final values for C_1 and d_1 those

[5] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. **63**, 229 (1928).

[9] F. G. Keyes, Zeits. f. physik. Chemie, *Cohen Festband*, 709 (1927).

[10] This value is a weighted mean of many experimental values derived from dielectric constant measurements. References are given in J. H. Van Vleck's *Theory of Electric and Magnetic Susceptibilities* (Oxford Press, 1932), p. 67.

[11] J. H. Van Vleck, reference 10, p. 205.

TABLE II.

Approx.	$d_1\times10^8$	C_1	$\eta_1\times10^6$ (193.16°A)	$\eta_1\times10^6$ (273.16°A)	$\eta_1\times10^6$ (373.16°A)
I	2.34	30.1	65.3	69.4	83.2
II	2.42	28.2	66.7	70.9	85.4
III	2.37	34.0	66.1	70.2	84.3
IV	2.40	30.2	66.4	70.8	85.1
V	2.38	31.7	66.0	70.3	84.5
VI	2.39	31.4	66.2	70.5	84.9

values which most closely reproduce the mean of the last three sets of values (values at 193.16°A, of course, are not considered although they have been calculated for the sake of completeness). On this basis the best values are $d_1=2.39\times10^{-8}$ cm and $C_1=30.6$, corresponding to η_1 values of 70.5×10^{-6} and 84.7×10^{-6}.

On the basis of Harteck's experimental results, therefore, we may represent the viscosity of atomic hydrogen from 0° to 100°C by

$$\eta_1=\frac{4.746\times10^{-6}T^{\frac{1}{2}}}{1+30.6/T}.$$

In like manner, we may calculate the diffusion coefficient for a mixture of atomic and molecular hydrogen from Eq. (10). For $d_1=2.39\times10^{-8}$ cm and $C_1=30.6$, C_{12} calculated from Eq. (9) is 31.9 so that the expression for the diffusion coefficient becomes

$$D_{12}=\frac{374.9T^{\frac{1}{2}}(1.0364-0.0303\alpha)}{P(1+31.9/T)},$$

where P is expressed in dynes/cm².

Kinetic studies on the relative recombination rate of atomic hydrogen and atomic deuterium[12] indicate that the diameters and attractive forces are equal for hydrogen and deuterium atoms. The coefficient of viscosity for atomic deuterium, therefore, should be $\sqrt{2}$ times that of atomic hydrogen because of the greater mass of the deuterium atom, or

$$D=\frac{6.711\times10^{-6}T^{\frac{1}{2}}}{1+30.6/T}.$$

In the case of *molecular* hydrogen and deuterium this $\sqrt{2}$ ratio for the coefficient of viscosity has been experimentally verified[13] indicating in this case, also, an equality of molecular diameters and attractive forces for the two isotopes. With this information it is possible to calculate the diffusion coefficients for all possible binary mixtures of atomic and molecular hydrogen and deuterium by substituting the proper values for M_1 and M_2 in Eq. (10) and in the Enskog expressions giving the concentration dependence of the diffusion coefficient. The result of such substitution is given in Table III. In each case x represents the mole fraction of the first (lighter) component. Since the concentration dependence is small, it makes little difference that in the above expressions α, the degree of dissociation, has been replaced by x, the mole fraction. The quantity, α, was used previously since slightly better agreement with Enskog's rigorous elastic sphere formula was obtained thereby. In view of the fact that we have assumed that the concentration dependence for our van der Waals gas is the same as that for a gas of hard elastic spheres, and since the use of α or x gives values within 0.2 percent on either side of those obtained from Enskog's formula, it seems desirable to make Eq. (10) general by the use of x.

TABLE III.

MIXTURE	DIFFUSION COEFFICIENT
D−D_2	$\frac{265.1T^{\frac{1}{2}}(1.0364-0.0303x)}{P(1+31.9/T)}$
H−D_2	$\frac{342.2T^{\frac{1}{2}}(1.0559-0.0541x)}{P(1+31.9/T)}$
D−H_2	$\frac{306.1T^{\frac{1}{2}}(1.0172-0.0x)}{P(1+31.9/T)}$
H−D	$\frac{400.4T^{\frac{1}{2}}(1.0364-0.0303x)}{P(1+30.6/T)}$

Although Harteck's relative viscosity values furnish an experimental basis for the present expressions only from 0° to 100°C, it seems quite probable that use of the formulas beyond this temperature range will give fairly accurate (one percent or better) values for the viscosity and diffusion coefficients. This prediction is based on the fact that the Sutherland expression for molecular hydrogen (with the corrected value of C) holds from −200° to +300°C and that atomic hydrogen may be regarded as a van der Waals gas with a diameter and attractive force almost equal to that of molecular hydrogen.

[12] I. Amdur, J. Am. Chem. Soc. **57**, 856 (1935).
[13] I. Amdur, J. Am. Chem. Soc. **57**, 588 (1935).

The Free Energy of Iodine and Hydrogen Iodide from Spectroscopic Data

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Partition functions have been calculated for HI, I_2 and I atom between 298.1 and 1500°K from spectroscopic data and the results have been fitted to a free energy equation of the usual thermodynamic form which may be differentiated and integrated to give change of heat content, specific heat and entropy for chemical reactions involving HI, I_2, I and H_2. The experimentally determined equilibrium constants for the reactions $I_2 \rightarrow 2I$ and $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$ have been compared with the theoretical equilibrium constants. For the latter reaction, it is shown that the results of Bodenstein may be in error due to incorrect temperatures. Reliable values have been given for the heat of dissociation of iodine and hydrogen iodide at 25°C.

CALCULATION of thermodynamic functions from spectroscopic data may be made with complete confidence since the statistical weights of the degenerate energy levels are now well understood. Moreover, the measurements of molecular spectroscopy are so exact that in most cases these calculated functions will far exceed the experimental ones in precision. The requisite partition functions have now been summed and discussed for a large number of molecules[1] including Cl_2 and HCl,[2] Br_2 and HBr[3] but the corresponding data for I_2 and HI[4] have not been given in detail.

In connection with experiments now completed in this laboratory on the rate of decomposition of deuterium iodide, it became necessary to calculate the equilibrium concentration of DI at various temperatures and we have therefore obtained the partition functions for I_2, HI and I atom and determined the free energy decrease and other thermodynamic functions for the reaction

$$HI \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}I_2 \qquad (1)$$

and the corresponding deuterium reaction. This paper is concerned with the hydrogen case while the corresponding data for DI as well as a discussion of the rates of the two reactions will appear later.

The method of calculating thermodynamic functions from spectroscopic data is well known and reference may be made to the reviews cited above for complete details. The partition functions are given by $Q = \Sigma p \exp(-E/kT)$, where p is the statistical weight of the energy level and summation is made over the required number of electronic, vibrational and rotational states. The energy, as obtained from spectroscopic data is a complicated function of v and $J(J+1)$, the vibrational and rotational quantum numbers, respectively. Once the Q functions and their derivatives are known the free energy, entropy and other properties follow by the well-known methods of statistical mechanics and thermodynamics. The laborious task of summing over all the energy levels has been simplified by several methods. We have found the procedure of Kassel[5] useful, especially for such a molecule as I_2 where a large number of vibrational levels must be summed.

The molecular constants for I_2 were taken from Jevons[6] and may be found in Table I along with those for HI, which were recalculated from the recent experiments of Nielsen and Nielsen,[7] who measured the fundamental and first harmonic

TABLE I.

	I_2	HI
B_0	3.73×10^{-2}	6.4576
D_0	-4.536×10^{-9}	-2.1013×10^{-4}
α	1.2×10^{-4}	1.725×10^{-1}
β	1.63×10^{-11}	—
ω_e	214.26	2309.55
$x_e\omega_e$	0.592	39.735

[1] For reviews of the subject, see Giauque, J. Am. Chem. Soc. **52**, 4808 (1930); Zeise, Zeits. f. Elektrochemie **39**, 758, 895 (1933); **40**, 662, 885 (1934). The latter author has compiled the available data for both diatomic and polyatomic molecules.

[2] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[3] Gordon and Barnes, J. Chem. Phys. **1**, 692 (1933).

[4] The free energy function for HI at a few temperatures has been given by Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Zeise (reference 1) has given the same functions for I_2 but has not discussed the experimental data critically as we do here.

[5] Kassel, J. Chem. Phys. **1**, 576 (1933); Phys. Rev. **43**, 364 (1933).

[6] Jevons, *Report on Band-Spectra of Diatomic Molecules* (University Press, Cambridge, 1932).

[7] Nielsen and Nielsen, Phys. Rev. **47**, 585 (1935).

TABLE II.

T	Q	$-(F^\circ-E_0^\circ)/T$
	I_2	
298.1	4,375.64	54.193
500	10,356.64	58.474
800	24,109.80	62.487
1000	36,595.51	64.425
1500	79,854.51	67.988
	HI	
298.1	32.6307	42.418
500	54.6738	46.012
800	89.0072	49.315
1000	114.0486	50.916
1500	187.4235	53.916
	I	
298.1	4	38.225
500	4	40.794
800	4	43.128
1000	4	44.237
1500	4	46.250

absorption bands of HI in the infrared. Their results are in agreement with the work of Czerny,[8] Salant and Sandow[9] and Kirkpatrick.[10] In accordance with the practice of Giauque and co-workers, we have used the natural constants given in the *International Critical Tables*.[11] The partition functions were calculated for both HI and I_2 at 298.1, 500, 800, 1000 and 1500°K and are given in Table II. Many intermediate values were also summed in order to test the interpolation formula which is described below. For the iodine atom, the normal state is an inverted ^2P level, with a doublet separation[12] of 7600 cm^{-1} and the contribution from this level is negligible up to several thousand degrees. The partition function for I atom is therefore independent of temperature in this range and is $Q=4$.

From the Q functions, the free energy for the molecule or atom may be obtained from the expression

$$-(F^\circ-E_0^\circ)/T=(3/2)R\ln M+(5/2)R\ln T+R\ln Q-7.267, \quad (2)$$

where M is the molecular or atomic weight and E_0° is the energy at the absolute zero. Following the usual custom, which is valid for temperatures above 25°C, the nuclear spin contributions have been excluded but for the homo-nuclear molecule, I_2, the Q function as calculated must be divided by two which has been done for the results given in Table II. The atomic weights for hydrogen and iodine were taken as 1.00778 and 126.932, respectively.[13]

Since interpolation for other temperatures is fairly laborious, the free energy functions obtained at the five temperatures mentioned above were fitted to an equation of the form

$$-(F^\circ-E_0^\circ)/T=a/T+b\log T+cT+dT^2+i, \quad (3)$$

which is suggested by thermodynamic considerations.[14] The constants in this equation are given for HI, I_2 and I atom as well as for H_2, the latter being taken from the free energy functions of Giauque[15] at the same five temperatures as for the other molecules. The results will be found in Table III. It is probably not safe to extrapolate these equations beyond 298.1 or 1500°K but over this entire range, the free energy function (3) is reproduced to within ±0.001 cal./mole as tested by calculation and comparison with about 15 points within this temperature range.

If the value of ΔE_0° is known for any particular reaction, it may be combined with equations of the form (3) for the individual reactants to obtain an equation of the same form, representing the free energy change of the reaction

$$-\Delta F^\circ/T=-\Delta(F^\circ-E_0^\circ)/T-\Delta E_0^\circ/T=R\ln K, \quad (4)$$

where K is the equilibrium constant at unit pressure. In accordance with the thermodynamic

TABLE III.

	HI	H_2
a	−108.672	114.572
b	14.6592	16.7648
c	7.649×10^{-4}	-5.410×10^{-4}
d	-4.0×10^{-10}	1.67×10^{-7}
i	6.2820	−17.2832
	I_2	I
a	180.778	−28.052
b	19.8028	11.1292
c	4.442×10^{-4}	1.907×10^{-4}
d	-6.87×10^{-8}	-4.09×10^{-8}
i	4.4605	10.7277

[8] Czerny, Zeits. f. Physik **44**, 235 (1927).
[9] Salant and Sandow, Phys. Rev. **37**, 373 (1931).
[10] Kirkpatrick, Phys. Rev. **49**, 104 (1936).
[11] Int. Crit. Tab., Vol. I, p. 16. The numerical constant of the free energy equation was taken as 7.267; $R=1.9869$; $hc/k=1.4324$.
[12] Turner, Phys. Rev. **27**, 397 (1926).
[13] Aston, *Mass-Spectra and Isotopes* (Longmans, Green and Co., New York, 1933).
[14] See, for example, Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Co., New York, 1932), particularly Chapter XV.
[15] Giauque, J. Am. Chem. Soc. **52**, 4816 (1932).

notation, we write Eq. (4) in the form

$$\Delta F^\circ/T=\Delta H_0/T-\Delta\Gamma_0 \ln T-\tfrac{1}{2}\Delta\Gamma_1 T -\tfrac{1}{6}\Delta\Gamma_2 T^2+I. \quad (5)$$

This equation, except for the uncertainty in the quantity, ΔE_0° will give the correct free energy change of the reaction to ± 0.001 cal./mole over the entire temperature range from 298.1 to 1500°K. It may also be differentiated and integrated to give changes in heat content, specific heat and entropy

$$\Delta H=\Delta H_0+\Delta\Gamma_0 T+\tfrac{1}{2}\Delta\Gamma_1 T^2+\tfrac{1}{3}\Delta\Gamma_2 T^3+\cdots, \quad (6)$$

$$\Delta C_p=\Delta\Gamma_0+\Delta\Gamma_1 T+\Delta\Gamma_2 T^2+\cdots, \quad (7)$$

$$\Delta S=\Delta\Gamma_0(\ln T+1)+\Delta\Gamma_1 T+\tfrac{1}{2}\Delta\Gamma_2 T^2-I. \quad (8)$$

We have not investigated the precision of any of these expressions by direct summation except the entropy equation which we discuss later but it seems likely that they will all give results of sufficient precision for most applications, although they are not as exact as the free energy equation. Their chief advantage lies in the avoidance of the tedious process of summation which is required for determining the entropy and other quantities from spectroscopic data.

The Dissociation of Iodine Molecule

The decomposition of molecular iodine into atoms has been studied by Starck and Bodenstein,[16] Braune and Ramstetter[17] and DeVries and Rodebush.[18] Gibson and Heitler[19] have shown that the experimental results of Starck and Bodenstein are in agreement with the statistical calculations. They assumed the iodine molecule to be a rigid rotator and a simple harmonic oscillator and added a slight correction term to account for anharmonicity but the exact partition functions as calculated here do not change their results by a very large amount. The value of ΔE_0° for this reaction has been given by Brown[20] from extrapolation of spectroscopic data as 1.535 ± 0.001 ev or $35{,}395\pm 23$ cal./mole.[21] This result when substituted into Eq. (4) is definitely inconsistent with the equilibrium data. Gibson and Heitler have rejected a similar result of 1.532 ev given by Kuhn[22] as too small and have preferred to take 1.544 ± 0.003 ev by extrapolation of the bands of Mecke.[23] Because of this uncertainty, we have used Eq. (4) and the experimental equilibrium constants to determine ΔE_0°, giving a result of $35{,}795\pm 100$ cal./mole. While this is definitely higher than any of the previous values it seems necessary if all of the experimental data are to be given equal weight. Combining this value of ΔE_0° with the proper constants from Table III and using Eq. (5) we obtain values for the coefficients of that equation as given in Table IV. A plot of $\log K$ against $1/T$ for all the experimental data is given in Fig. 1, which is seen to be a straight line. A more certain value of ΔE_0° will only result in a shift of the whole curve parallel to itself in either direction. The equilibrium constant is given by

Table IV.

	$I_2\rightarrow 2I$	$HI\rightarrow\frac{1}{2}H_2+\frac{1}{2}I_2$
ΔH_0	36.032	715.48
$\Delta\Gamma_0$	1.0664	1.5741
$\Delta\Gamma_1$	-1.256×10^{-4}	-1.6266×10^{-3}
$\Delta\Gamma_2$	-7.86×10^{-8}	2.973×10^{-7}
I	−16.9949	12.6934

$$K_p=4\alpha^2 P/(1-\alpha^2), \quad (9)$$

where α is the degree of dissociation of iodine and P is the pressure in atmospheres.

Using Eq. (6), we obtain for the heat of dissociation of iodine into atoms at 298.1°K

$$\Delta H_{298.1}=36{,}343\pm 100 \text{ cal./mole}$$

and from Eq. (8)

$$\Delta S_{298.1}=24.097 \text{ cal./degree per mole.}$$

By direct summation at this temperature, we have obtained $S_{298.1}(I_2)=62.29$; $S_{298.1}(I)=43.19$; $\Delta S_{298.1}=24.09$ in satisfactory agreement with Eq. (8). The value for I_2 is in exact agreement with the calculations of Giauque,[24] who used an approximate method for determining the partition functions.

[16] Starck and Bodenstein, Zeits. f. Elektrochemie **16**, 961 (1910); **22**, 327 (1916).
[17] Braune and Ramstetter, Zeits. f. physik. Chemie **102**, 480 (1922).
[18] DeVries and Rodebush, J. Am. Chem. Soc. **49**, 656 (1927).
[19] Gibson and Heitler, Zeits. f. Physik **49**, 465 (1928).
[20] Brown, Phys. Rev. **38**, 709 (1931).
[21] We take 1 ev = 23,085.5 cal./mole.
[22] Kuhn, Zeits. f. Physik **39**, 77 (1926).
[23] Mecke, Ann. d. Physik **71**, 103 (1923).
[24] Giauque, J. Am. Chem. Soc. **53**, 507 (1931).

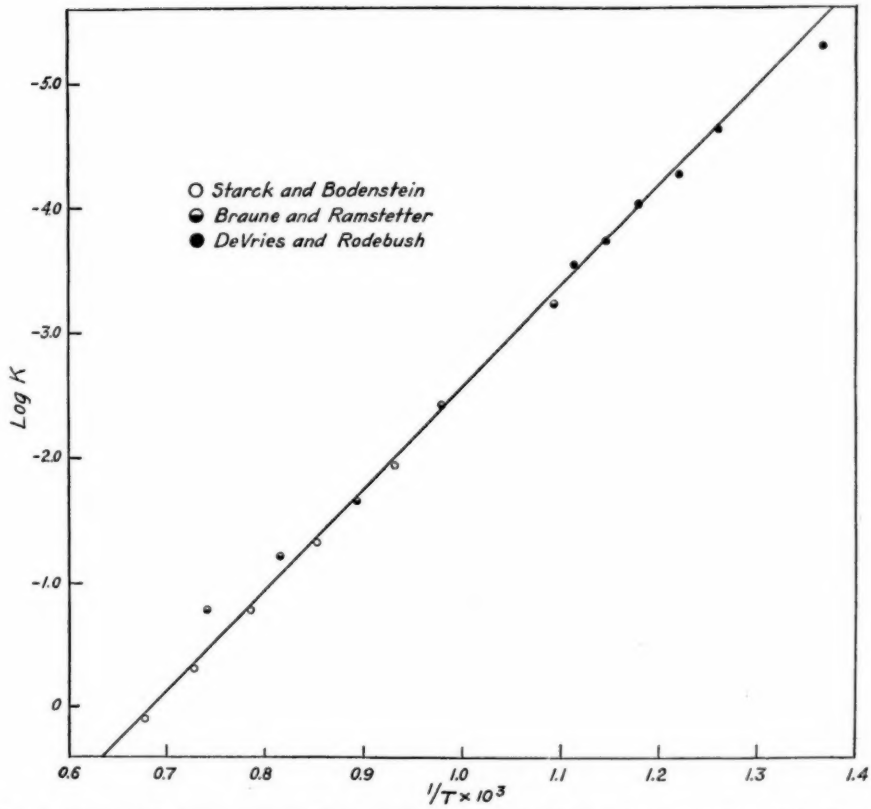

FIG. 1. The equilibrium constant for the reaction: $I_2 \rightarrow 2I$. Theoretical curve from Eq. (5) and Table IV; experimental points from various authors.

THE DISSOCIATION OF HYDROGEN IODIDE

The thermal equilibrium between hydrogen, iodine and hydrogen iodide has been studied by Bodenstein[25] and is generally considered to be the most carefully investigated gaseous equilibrium to be found in the literature. In addition to the earlier experiments of Hautefeuille[26] and Lemoine,[27] the equilibrium has also been studied at 1022 and 1217°C by von Falckenstein[28] and near room temperatures by Stegmüller,[29] using an electromotive force method. More recently, Urey and Rittenberg[30] have studied the equilibrium with mixtures of hydrogen and deuterium and have shown that the constants obtained from the spectroscopic data for the reaction

$$H_2+2DI \rightarrow D_2+2HI \qquad (10)$$

are in agreement with the experimentally determined ones. The latter authors have also given two measurements with hydrogen iodide alone.

For this reaction, the value of ΔE_0° is still more uncertain than for the iodine decomposition. We have therefore followed the same procedure as above to determine this quantity although we have used only the data of Bodenstein and the two points of Rittenberg and Urey. Following a suggestion of Haber,[31] however, we first correct the measured equilibrium constants for the dissociation of iodine molecules into atoms which is not very great but should not be neglected at the highest temperatures. If ξ is the concentration of hydrogen or iodine at

[25] Bodenstein, Zeits. f. physik. Chemie **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899); Habilitationsschrift, Heidelberg, 11–36, W. Engelmann, Leipzig, 1899.
[26] Hautefeuille, Comptes rendus **64**, 608 (1867).
[27] Lemoine, Ann. chim. phys. (5) **12**, 145 (1877).
[28] von Falckenstein, Zeits. f. physik. Chemie **68**, 270 (1909); **72**, 113 (1910).
[29] Stegmüller, Zeits. f. Elektrochemie **16**, 85 (1910).
[30] Rittenberg and Urey, J. Am. Chem. Soc. **56**, 1885 (1934).
[31] Haber, *Thermodynamics of Technical Gas-Reactions* (Longmans, Green and Co., New York, 1908).

equilibrium and α is the percentage decomposition of iodine into atoms, the corrected equilibrium constant for the reaction (1) is given by

$$K' = \xi(1-\alpha)^{\frac{1}{2}}/2(1-\xi) = K(1-\alpha)^{\frac{1}{2}}, \quad (11)$$

where K is Bodenstein's constant.

A more serious difficulty is the uncertainty of Bodenstein's temperatures. His experiments cover the temperature range between 283 and 508°C and several thermostats were used. A number of temperatures were obtained with a sulfur vapor bath, the temperature being varied by boiling the sulfur under reduced pressures. The temperature was determined by measuring the vapor pressure of the sulfur with a manometer, the pressure-temperature curve for sulfur having been previously determined by means of calibrated mercury thermometers. Comparison with the present vapor pressure curve[32] of sulfur shows some divergence from the temperatures as given by Bodenstein and since he gave the observed pressure in each case, it is possible to make corrections. The present vapor pressure curve of sulfur may be in error by as much as 3° at the lowest temperature but since Bodenstein's temperature differs at this point by 10°, the corrected temperatures as given in Table V seem more nearly correct than those given by Bodenstein. The boiling point of mercury was used for another temperature and this is apparently correct while PS_5 was used in another thermostat and we have changed this temperature from 508° to 514°C in accordance with the *International Critical Tables*, although this is more uncertain than the sulfur points. All of his other temperatures were measured with a mercury thermometer and naturally nothing can be said of their errors, if any. The two points of Urey and Rittenberg mentioned above are apparently correct since the temperatures were directly measured with a thermocouple. The corrected temperatures and equilibrium constants corrected in accordance with Eq. (11) for the dissociation of iodine are given in Table V.

Using these corrected temperatures only, we have then used Eq. (4) to calculate ΔE_0° as before. The value obtained is

$$\Delta E_0^\circ = 971.83 \pm 13.65 \text{ cal./mole.}$$

[32] Int. Crit. Tab., Vol. III, p. 201.

TABLE V.

$T_{Bod.}$	$T_{corr.}$	log K' (exp.)	log K' (calc.)
781	787	−0.8002	−0.8121
760	—	−0.8163	−0.8268
—	*741	−0.8328	−0.8377
716	717	−0.8513	−0.8523
700	700	−0.8618	−0.8630
683	684	−0.8765	−0.8736
—	*671	−0.8840	−0.8826
666	671	−0.8876	−0.8826
647	657	−0.9004	−0.8925
629	—	−0.9179	−0.9179
601	—	−0.9350	−0.9361
575	—	−0.9552	−0.9588
556	—	−0.9639	−0.9765

$T_{Bod.}$ are Bodenstein's experimentally determined temperatures in °K, $T_{corr.}$ are the temperatures which could be corrected as explained above.
* Data of Rittenberg and Urey.

This constant has then been used in Eq. (5) to give the free energy decrease of the reaction, the constants in the equation being found in Table IV. The same remarks that were made above as to precision apply also in this case.

Using Eq. (6) we obtain

$$\Delta H_{298.1} = 1113 \pm 15 \text{ cal./mole.}$$

If we take the heat of sublimation of iodine as 7438 cal./mole as given by Giauque,[24] we obtain -6325 ± 15 cal./mole for the heat of dissociation of HI into hydrogen and solid iodine. This may be compared with the calorimetric determinations of Thomsen and Berthelot[33] who found 6000 and 6300 cal./mole, respectively. A recent calorimetric determination by Günther and Wekua[34] for the reaction

$$HI(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g) + \tfrac{1}{2}I_2(s) \quad (12)$$

gave $\Delta H = 27{,}966 \pm 50$ cal./mole at room temperture. Assuming the latter to be 25°C and combining with the heat of formation of HCl, given by Giauque and Overstreet[2] as $22{,}028 \pm 10$ cal./mole gives 5942 ± 50 cal./mole for the heat of decomposition of HI. This value cannot be combined with the spectroscopic data to give agreement with the experimental equilibrium constants[35] and it seems evident that some unsuspected source

[33] Lewis and Randall, reference 14, page 525.
[34] Günther and Wekua, Zeits. f. physik. Chemie A154, 193 (1931).
[35] Zeise, reference 1, has also reached a similar conclusion.

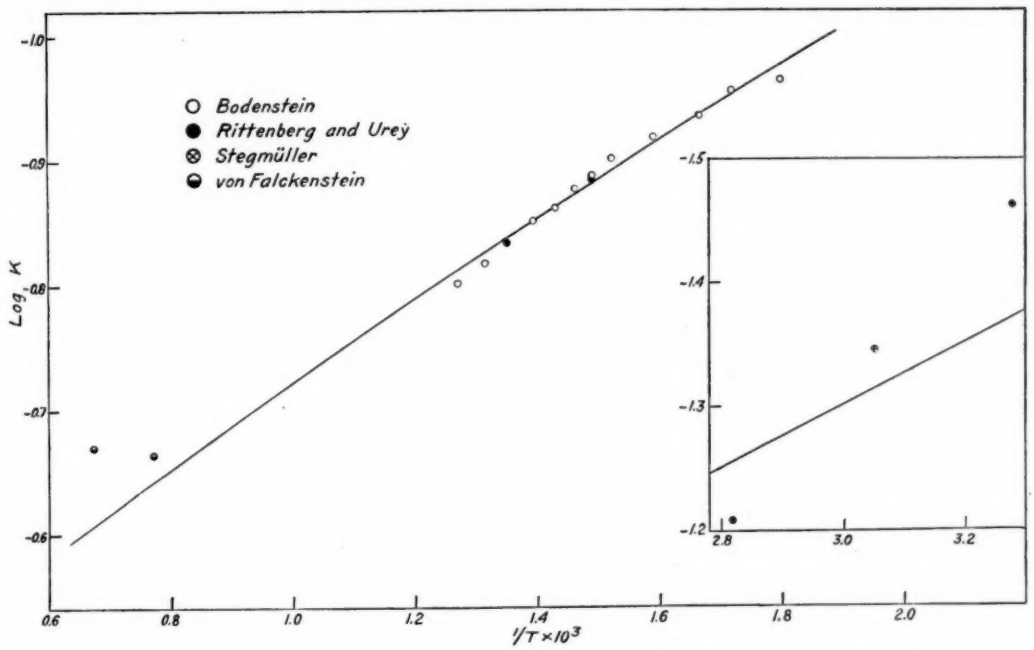

FIG. 2. The equilibrium constant for the reaction: $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$. Theoretical curve from Eq. (5) and Table IV; experimental points from various authors.

of error was present in these calorimetric determinations.

Using Eq. (8) we find

$$\Delta S_{298.1} = -2.623 \text{ cal./degree per mole.}$$

Summation gives for HI at the same temperature the value -49.36 and combining with $S(H_2) = 31.23$ from Giauque[15] and the entropy of I_2 as given above, we obtain $\Delta S_{298.1} = -2.60$, in satisfactory agreement with our interpolation formula (8). Giauque[24] using a rigid molecule for HI, obtained $S(HI) = 49.8$ and since he used the same values as above for H_2 and I_2, he finds $\Delta S = -3.04$. The difference is due entirely to his value for HI. Experimentally, Giauque and Wiebe,[36] find $S_{298.1}(HI) = 49.5$.

The equilibrium constants as calculated by Eq. (4) and the constants given in Table IV will be found in Table V and a plot of $\log K$ against $1/T$ in Fig. 2. We have also included there the results of von Falckenstein and Stegmüller. The former were apparently incorrectly changed by the author for the decomposition of I_2 and the possibility of a reaction between Pt and I_2 was not considered as pointed out by Jellinek and Uloth,[37] which undoubtedly accounts for the divergence from the calculated curve, although the values of K' as plotted here do not help the agreement very much. The results of Stegmüller are probably in error because of neglect of liquid junction potentials as stated by Lewis and Randall.[33] On the other hand, the points of Bodenstein and Rittenberg and Urey are in good agreement with the theoretical curve. Consideration of the errors involved shows that an error of 0.5 percent in the analysis would account for the divergence of the point which lies furthest from our theoretical curve. However, if one drew the best curve through all of the experimental points, the slope of the line would be quite different from the one we have chosen from the statistical calculations. Although Fig. 2 has a slight curvature and is not a straight line like Fig. 1, the spectroscopic data can certainly not be so adjusted to give the

[36] Giauque and Wiebe, J. Am. Chem. Soc. **51**, 1441 (1929).

[37] Jellinek and Uloth, Zeits. f. anorg. Chemie **151**, 161 (1926).

extreme curvature required by the experimental points but can only be shifted parallel to itself because of the uncertainty in $\Delta E_0°$. The slight curvature in Fig. 2, mentioned above is probably due to the anharmonic terms and the rotational stretching terms in the energy expression for HI which also explains why Fig. 1 is a straight line since these quantities are nearly negligible for a heavy molecule like iodine.

Note added in proof: Further consideration shows that the attempted correction of Bodenstein's temperatures may not be justified as his experimental temperatures with the sulfur baths fit the theoretical curve as well as the corrected ones. However, this does not affect any of the calculations made above since either set of temperatures will give the same $\Delta E_0°$ within the probable error stated. The doubtful points are thus the ones at the lowest and highest temperatures which may be explained by errors in analysis or what is more likely some further uncertainty in the experiments.

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The Isotope Effect in the Evaporation of Lithium, Potassium and Rubidium Ions

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Abundance ratio measurements are necessarily complicated by the possibility of an isotope effect at the source. In the emission of positive thermions of lithium, potassium and rubidium the extent to which the ion ratio represents the atom ratio within the source can be estimated by observing the change in the abundance ratio as a function of the percent of alkali evaporated. In the case of lithium an initial ratio of $Li^7/Li^6 = 11.60$ was observed; the abundance ratio followed the computed ratio for ideal evaporation until the lithium was 40 percent exhausted, beyond which it fell below the ideal value. The abundance ratios of $K^{39}/K^{41} = 14.22$ and $Rb^{85}/Rb^{87} = 2.59$ remained almost unchanged during the process of exhaustion. It is apparent therefore that a correction factor needs to be applied to the ion abundance ratio for lithium, but is unnecessary for potassium and for rubidium. The atomic weights computed from the abundance ratios are Li = 6.939, K = 39.094 and Rb = 85.46.

AN accurate estimation of isotope abundance ratios from mass-spectrographic measurements necessarily involves the question of an isotope effect at the positive ion source. The extent to which the ion ratio represents the true abundance ratio is amenable to a comparatively simple test in the case where positive thermions are used as the ion source.

In the mass spectrograph which was described recently,[1] heated platinum disks impregnated with alkali were used as the source of positive ions. These ion emitters were prepared by coating the platinum with a water paste made from the salt to be tested. These coated disks can be used directly as positive ion emitters, although platinum impregnated with alkali is in general the more satisfactory source. This impregnation is readily accomplished by heating the disk to dull redness in contact with the adhering coating for about half an hour; the coating is then removed by scraping and washing with distilled water. During the heating process the platinum dissolves sufficient alkali to become an excellent emitter of positive ions.

The test for a preferential isotope effect in the emission of alkali ions was made by observing the changes in the abundance ratio as a function of the fraction of the alkali evaporated. This fraction was obtained from a determination of the time and current necessary for the complete exhaustion of the less abundant isotope; the abundance ratio was measured at regular intervals during the exhaustion period.

RESULTS

The procedure just described yields the abundance ratio as a function of the less abundant isotope evaporated from the platinum. Curve *A*, Fig. 1 shows a representative run obtained with lithium. The initial abundance ratio, $Li^7/Li^6 = 11.6$, is the same as that reported previously.[2] During the exhaustion period it was necessary

[1] A. Keith Brewer, J. Am. Chem. Soc. **58**, 365 (1936).

[2] A. Keith Brewer, Phys. Rev. **47**, 571 (1935).

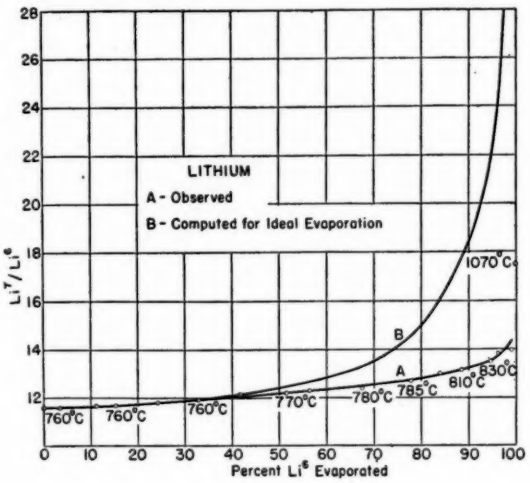

FIG. 1.

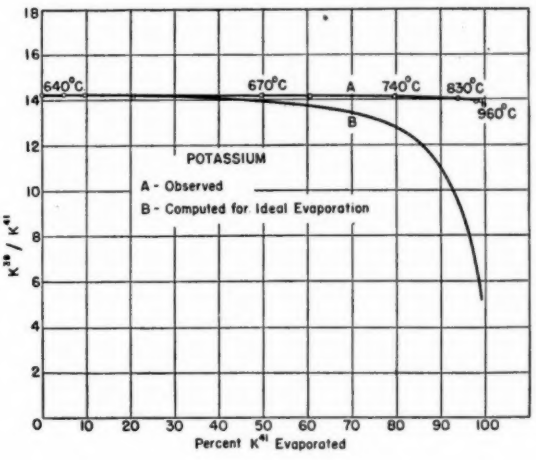

FIG. 2.

to raise the disk temperature to obtain sufficient current to measure the abundance ratio; the approximate temperatures at which the ratios were determined are shown accompanying the points. Temperature, in itself, appears to have little effect on the abundance ratio since it remained the same over the range of positive ion currents that could be investigated.

The results obtained with potassium are shown in line *A*, Fig. 2. The abundance ratio, $K^{39}/K^{41}=14.22$, is essentially the same as that obtained from most mineral sources. This ratio remained almost unchanged throughout the evaporation period, dropping to 14.1 for about 90 percent emitted, and to 13.8 for the last traces of potassium left in the platinum.

The initial abundance ratio obtained from rubidium is $Rb^{85}/Rb^{87}=2.59\pm0.01$. This is essentially the same as 2.59 ± 0.04 obtained previously[3] but is lower than the value of $Rb^{85}/Rb^{87}=2.68\pm0.02$ recently reported by Nier,[4] using a different type of ion source. Since the previous value was obtained with an entirely different spectrograph and rubidium salt, it seems definite that the abundance ratio from this type of source is very close to $Rb^{85}/Rb^{87}=2.59$.

The abundance ratio as a function of the percent of Rb^{87} evaporated is shown in Fig. 3. No measurable change was observed during the exhaustion period. The conspicuous fact to be observed in the above results is that potassium and rubidium show almost no isotope effect while lithium shows a marked shift in the abundance ratio during the evaporation period.

Discussion of Results

The thermionic emission of positive ions from platinum impregnated with alkali offers two possibilities for the exhibition of an isotope effect: First, through a difference in the rate of diffusion to the surface, and second, through a difference in the rate of escape from the surface as positive ions.

Assuming that the alkali atoms are at liberty to diffuse freely through the platinum, the number N of atoms striking unit area of the bounding surface in unit time with a velocity component between u and $u+du$ normal to the surface is

$$N(u)du=n(m/2\pi kT)^{\frac{1}{2}}ue^{-mu^2/2kT}du, \qquad (1)$$

where n is the concentration of alkali atoms per unit volume of platinum and m is their mass.[5]

The total number of atoms striking the bounding surface is the integral of the above expression from 0 to ∞ while the number escaping as ions is the integral between u_0 and ∞ where u_0 is the minimum velocity for escape. Thus N^+, the number of positive ions escaping per second per sq. cm is

[3] A. Keith Brewer and P. D. Kueck, Phys. Rev. **46**, 894 (1934).

[4] A. O. Nier, Phys. Rev. **49**, 272 (1936).

[5] L. B. Loeb, *Kinetic Theory of Gases* (McGraw-Hill).

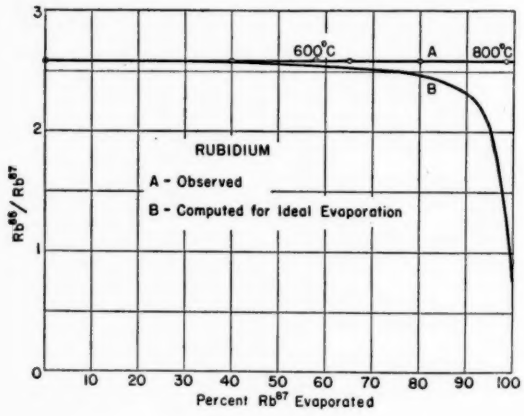

FIG. 3.

$$N^+ = n(kT/2\pi m)^{\frac{1}{2}} e^{-mu_0^2/2kT}. \quad (2)$$

This equation can be applied directly to the case of lithium, a similar equation being written for each isotope. This gives

$$n_7/n_6 = N_7^+/N_6^+ (m_7/m_6)^{\frac{1}{2}} e^{-(m_6u_6^2 - m_7u_7^2)/2kT} \quad (3)$$

for the abundance ratio of the isotopes in the metal (n_7/n_6) as a function of the ratio of the positive ion currents (N_7^+/N_6^+).

From this expression it will be seen that if perfect mixing of the lithium atoms takes place within the platinum the observed ion ratio must be multiplied by the square root of the ratio of the isotope masses to correct for the difference in the collision frequency with the bounding surface, and also by an exponential factor to correct for a possible difference in the work functions.

While it cannot be stated with certainty that the work function for the two isotopes is the same, the difference must be negligible since the ionization potential is the same for each to within one-millionth of a volt. This being the case the exponential factor becomes equal to one and can be neglected. In consequence it seems apparent that the ratio of the isotope atoms leaving the surface as positive ions is proportional to the concentration at the bounding surface. Any isotope effect that may exist, therefore, comes from the difference in the collision frequency with the surface.

Assuming the exponential factor in Eq. (3) is equal to unity and that perfect mixing takes place in the platinum disk used in these experiments it is possible to compute the abundance ratio that should exist for the escaping ions at different stages of the evaporation of the alkali. Lines *B* in Figs. 1, 2 and 3 are so computed for various percentages of the lesser isotopes evaporated. A comparison of the observed *A* lines with the computed *B* lines gives, in consequence, the extent to which perfect mixing and ideal diffusion take place within the platinum source.

A possible explanation of the fact that lithium exhibits an isotope effect while potassium and rubidium do not may be found in the dimensions involved. The radius of the lithium ion is 0.6A, potassium is 1.33A, and rubidium is 1.48A; the radius of the platinum atom in the metal is 1.39A. A solid solution of potassium or rubidium in platinum, since the dimensions are essentially the same, will, therefore, be of the replacement type in which the alkali atom replaces a platinum atom in the metal lattice. In this case diffusion takes place step by step from lattice to lattice with little or no opportunity for mixing; an isotope effect, in consequence, is not to be expected. The lithium atom, on the other hand is small compared to the separation of the platinum atoms; here interstitial solution is possible in which the lithium atoms do not enter into the metal structure but actually penetrate the platinum lattice. The lithium atoms are in this case free to move more or less at random through the platinum mass, thus permitting a more ideal mixing than is possible in a replacement solution where the dissolved atoms are confined to fixed positions. This mixing is not perfect, however, since Fig. 1 shows that the computed and observed curves begin to diverge before the alkali is half exhausted. It has been pointed out that not all atoms colliding with the bounding surface will escape as positive ions, but only those of high energy content. This means that lithium atoms will tend to concentrate in the surface region thus congesting the interstitial space and obstructing the freedom of collision.

Results obtained with coated lithium aluminum silicate emitters lead to a conclusion of similar character. The abundance ratio remained constant at 11.60 for some time, then rose to a final value of 13.88 after prolonged heating above the fusion point.

The various methods that have been employed for the separation of isotopes have been discussed by Aston.[6] The present results suggest some of the conditions under which thermionic emission can be utilized for this purpose. It is evident that when the atoms to be emitted as thermions do not have to conform to any definite lattice structure within the emitter conditions approaching ideal evaporation may be realized. Emission from fused salts show an appreciable isotope effect. In the case of metallic emitters the positive ions which have been held in interstitial solution exhibit a preferential emission of the light isotope ions while those held in replacement solution show little if any effect.

The values for the abundance ratios which have just been presented may now be employed in estimating the atomic weights of these elements by the method recently described in detail for potassium.[7] The atomic weight of 39.094 obtained for potassium remains unchanged. With 1.00027 for the conversion factor from the physical to the chemical scale and -8.2 for the packing fraction, the atomic weight of rubidium comes out to be 85.46. This value compares favorably with 85.44 accepted by the committee on atomic weights and 85.48 recently obtained by Archibald, Hooley and Phillips.[8]

In estimating the atomic weight of lithium it is necessary to apply a correction for the isotope effect of free evaporation to the abundance ratio obtained from fresh filaments. Assuming this correction is initially that for ideal evaporation the abundance ratio becomes $11.60\sqrt{7/6}=12.52$. With this corrected value for the abundance ratio and 7.0146 and 6.0146 obtained by Bainbridge[9] for the isotope masses the atomic weight comes out to be 6.939. The most recent values for the isotope masses[10] of $Li^6=7.0180$ and $Li^6=6.0167$ lead to 6.942 for the atomic weight. Both these values are in close agreement with the accepted value of 6.940.

[6] F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold & Co., London, 1933).
[7] A. Keith Brewer, J. Am. Chem. Soc. **58**, 370 (1936).
[8] Archibald, Hooley and Phillips, J. Am. Chem. Soc. **58**, 70 (1936).
[9] K. T. Bainbridge, Phys. Rev. **44**, 56 (1933).
[10] M. L. Oliphant, Nature **137**, 396 (1936).

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Quantum-Mechanical Treatment of Helium Hydride Molecule-Ion HeH^+

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Helium hydride molecule-ion has been treated by the variation method, including ionic and polarization terms in the variation function and varying the effective nuclear charge. The equilibrium internuclear distance is found to be $1.57a_0$. Fitting a parabola to the lower part of the best potential energy curve leads to a value of 0.43 megadyne/cm for the force constant and a value of 2800 cm^{-1} for the fundamental vibration frequency. The minimum energy obtained for the system is $-5.844W_H$, which, when subtracted from the best value for the energy of the helium atom using the same type of variation function, gives a value for the dissociation energy of 2.02 ev. The doubly charged ion, HeH^{++}, is found to be unstable.

SINGLY charged helium hydride molecule-ion has been known[1] for many years from mass spectroscopic investigations of helium hydrogen mixtures. Its position with respect to that of $H^2H^2H^{1+}$ in the mass spectrograph has been used to determine accurately the mass of the deuteron.[2] Spectroscopic work has not shown the existence of this ion.

The only previous quantum-mechanical discussion of HeH^+ is a variation treatment made by Glockler and Fuller.[3] They consider two problems: (1) The interaction of a proton with an excited helium atom, the wave function for the electrons being $\psi_1=ae^{-\alpha r_1}$ and $\psi_2=(b+cr_2)e^{-\beta r_2}$; and (2) the interaction of a hydrogen atom with a singly ionized helium atom, the wave functions

[1] F. W. Aston, *Isotopes*, Both editions; T. R. Hogness and E. C. Lunn, Phys. Rev. **26**, 44 (1925).
[2] K. T. Bainbridge, Phys. Rev. **44**, 57 (1933).
[3] G. Glockler and D. L. Fuller, J. Chem. Phys. **1**, 886 (1933).

for the electrons being $\psi_1 = ae^{-\alpha r_{a1}}$ and $\psi_2 = be^{-\beta r_2}$. When in the first case α and β are put equal to 2 and 0.7, respectively, the interaction is repulsive at all distances. The functions ψ_1 and ψ_2 are the 1*s* and 2*s* hydrogen-like wave functions, the helium atom being approximately in the first excited state. In case two α and β are put equal to 2 and 1, the resulting potential energy curve has a minimum of 8.1 ev at $1.3a_0$. In this calculation the unsymmetrical Sugiura-type integral was neglected. As pointed out by Glockler and Fuller, including this integral will raise the energy by an undetermined amount.

The above calculation is not evidence for the existence of HeH^+. The dissociation energy, 8.1 ev, obtained by making the above approximation, is with respect to the dissociation products hydrogen atom and helium ion, while the difference in the ionization potentials of hydrogen and helium is 10.9 ev. Under these conditions the molecule would be unstable with respect to dissociation into a helium atom and a hydrogen ion. To prove the stability of the molecule it is necessary to show that for some intermediate internuclear distance the energy of the molecule is less than the energy of the helium atom.

The variational integral

$$W = \int \Psi^* H \Psi d\tau / \int \Psi^* \Psi d\tau$$

gives an upper limit for the energy of a system. Ψ is an approximate wave function. H is the Hamiltonian operator and in this case is

$$H = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{2e^2}{r_{a1}} - \frac{2e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{2e^2}{R}. \quad (1)$$

When a variation function of the form $\Psi = \sum_{n=1}^{m} c_n \psi_n$ is used, the condition that W be a minimum with respect to the constants c_n is that the determinantal equation $|H_{ij} - \Delta_{ij} W| = 0$ (Eq. (1)) be satisfied,[4] where $H_{ij} = \int \psi_i H \psi_j d\tau$ and $\Delta_{ij} = \int \psi_i \psi_j d\tau$. The approximate energy for the ground state will be the lowest root of this equation. The constants, c_n, are obtained by solving the set of linear equations $\sum_{j=1}^{m} c_j (H_{ij} - \Delta_{ij} W)$, $i = 1, 2, \cdots m$. Most of the integrals required in evaluating H_{ij} and Δ_{ij} were used by Rosen[5] and Weinbaum[6] in discussing the hydrogen molecule. Dr. Weinbaum has not published his integrals but kindly placed them at my disposal. The integrals used in this calculation, not tabulated by Rosen,[5] are given in the appendix.

The variation functions used here are composed of the following functions:

$$\begin{aligned} a(1) &= (Z^3/\pi a_0^3)^{\frac{1}{2}} e^{-Zr_{a1}/a_0}, \\ b(1) &= (Z^3/\pi a_0^3)^{\frac{1}{2}} e^{-Zr_{b1}/a_0}, \\ a'(1) &= (Z^5/\pi a_0^5)^{\frac{1}{2}} r_{a1} \cos\theta_{a1} e^{-Zr_{a1}/a_0} \end{aligned} \quad (2)$$

and the same functions for electron (2). Each function is normalized to unity. $a(1)$ is the ground state wave function for a hydrogenic atom of nuclear charge Z, and satisfies the equation

$$\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{Ze^2}{r_{a1}}\right) a(1) = -Z^2 W_H a(1)$$

where $W_H = (e^2/2a_0)$. $a'(1)$ is a first excited wave function for a hydrogenic atom of nuclear charge $2Z$ and satisfies the equation

$$\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{2Ze^2}{r_{a1}}\right) a'(1) = -Z^2 W_H a'(1).$$

This form of $a'(1)$ was used by Rosen[5] in introducing polarization into the hydrogen molecule calculation. It is very convenient as it leaves the exponents in $a(1)$ and $a'(1)$ identical making the calculation of integrals much simpler. In the present calculation the same effective nuclear charge, Z, is used in each term of the variation functions. This is done to eliminate the necessity of calculating the unsymmetrical Sugiura integral and other integrals. This procedure was adopted by Pauling[7] in treating the helium molecule-ion He_2^+.

[4] See for example Pauling and Wilson, *Introduction to Quantum Mechanics*.

[5] N. Rosen, Phys. Rev. **38**, 2099 (1931).
[6] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).
[7] Linus Pauling, J. Chem. Phys. **1**, 56 (1933).

It is evident that the stable state of the molecule is a singlet state so we shall require the variation function to be symmetric in the spatial coordinates of the two electrons (and antisymmetric in the spin coordinates). In the following paragraphs we shall calculate the energy of the systems for several such variation functions. It will be found possible, by taking a linear combination of the lowest lying states for simple wave functions, to obtain a calculated value of the energy of the molecule that is lower than the experimental value for the helium atom.

1. Normal Helium Atom and Proton

The most stable state for the system for a single wave function of the types we are considering, Eq. (2), is the state helium atom and proton. It will therefore be necessary, if the lowest value of the energy is desired, to include this state in the calculation. Taking as the electronic wave function of the system $\Psi=a(1)a(2)$, Eq. (1) for the energy becomes

$$W=\int \Psi^* H\Psi d\tau$$

$$=\left\{2Z^2-2Z\left[\frac{27}{8}-2e^{-2\rho}\left(1+\frac{1}{\rho}\right)\right]\right\}W_H,$$

where $\rho=ZR/a_0$. This interaction is repulsive at all distances and is shown by curve C, Fig. 1 for the case that $Z=27/16$. When ρ equals infinity this expression becomes the familiar expression for the energy of a helium atom for hydrogen-like wave functions with variable effective nuclear charge, $W=(2Z^2-27Z/4)W_H$. This energy is a minimum when $Z=27/16$ then $W=-5.695W_H$. The experimental value and the value calculated by Hylleraas[8] for the helium atom is $-5.807W_H$.

2. Hydrogen Atom and Helium Ion

The symmetric variation function,

$$\Psi=a(1)b(2)+a(2)b(1),$$

corresponds to an electron pair bond between the two atoms. The energy, is shown by curve B in Fig. 1 for the case that $Z=27/16=1.69$. This energy can be minimized with respect to Z for each value of ρ. When this is done a value of W only 0.04 percent lower than that for $Z=27/16$ is obtained, the effective charge then being equal to 1.72. When ρ equals infinity the energy becomes $W=(2Z^2-6Z)W_H$ which is a minimum when $Z=3/2$ and $W=-4.5W_H$. The correct value for the sum of the energies of a hydrogen atom and a helium ion is $-5W_H$. This discrepancy is due to the fact that we have taken the same effective charge on the two atoms.

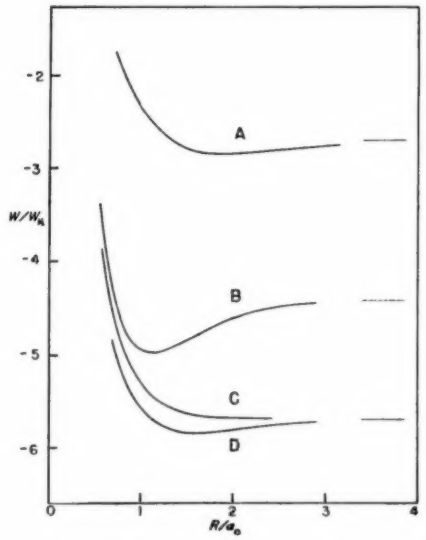

FIG. 1. Potential energy curves. A, $\Psi=a(1)a'(2)+a'(1)a(2)$; B, $\Psi=a(1)b(2)+b(1)a(2)$; C, $\Psi=a(1)a(2)$; D, $\Psi=a(1)a(2)+k_1(a(1)b(2)+b(1)a(2))+k_2(a(1)a'(2)+a'(1)a(2))$.

This calculation is the same as that made by Glockler and Fuller except that here the same effective nuclear charge is used on both atoms and consequently all the integrals can be calculated. This curve indicates the existence of a metastable attractive state for HeH^+.

3. Excited Helium Atom and Proton

The variation function

$$\Psi=a(1)a'(2)+a'(1)a(2),$$

in conjunction with $a(1)a(2)$, will be used to represent a polarized helium atom. The potential energy corresponding to the variation function $a'(1)a(2)+a(1)a'(2)$ alone is shown by curve A in Fig. 1 for the case that $Z=27/16$. This curve

[8] E. A. Hylleraas, Zeits. f. Physik 65, 209 (1930).

is higher than that for the corresponding triplet state, $a'(1)a(2)-a(1)a'(2)$, but the triplet state does not combine with the more important singlet states, nondiagonal matrix elements being equal to zero, so cannot be used. When the energy for the singlet state is minimized with respect to the effective nuclear charge, the energy curve is lowered by about $0.35W_H$, the corresponding value of the effective nuclear charge at the minimum being 1.26.

4. Combination of §§1 and 3

Using $\Psi=a(1)a(2)+k(a'(1)a(2)+a(1)a'(2))$ as a variation function, the energy appears as a root of a quadratic secular equation, Eq. (1). The result of solving the equation is shown by curve B in Fig. 2 for the case that the effective nuclear charge is 27/16. It is not possible to minimize easily with respect to the effective nuclear charge so the quadratic is merely solved for several values of the effective charge. It is found that the energy is worse for any value of the effective charge much different than 27/16. The minimum energy for this curve is $W=-5.750$ at $R=1.60a_0$. The normalized function is

$$\Psi=0.99a(1)a(2)+0.13(a(1)a(2)+a(1)a'(2)).$$

The best value of the energy of the system at R equals infinity for this type of variation function is $-5.695W_H$, giving for the dissociation energy of the molecule $0.055W_H$ or 0.74 ev. The stabilization resulting from the use of this variation function can be attributed to a polarization of the helium atom.

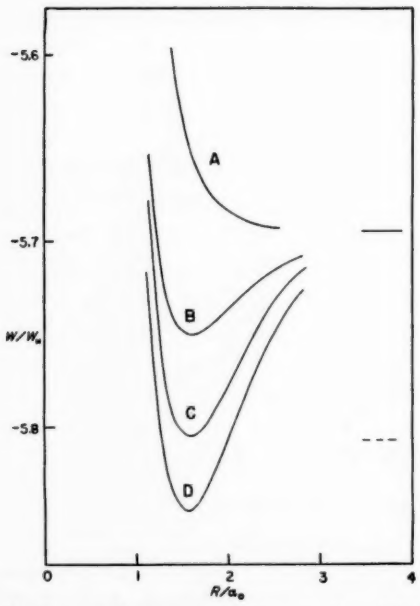

FIG. 2. Potential energy curves. A, $\Psi=a(1)a(2)$; B, $\Psi=a(1)a(2)+k(a(1)a'(2)+a'(1)a(2))$; C, $\Psi=a(1)a(2)+k(a(1)b(2)+b(1)a(2))$; D, $\Psi=a(1)a(2)+k_1(a(1)b(2)+a(2)b(1))+k_2(a(1)a'(2)+a'(1)a(2))$. The dashed line represents the experimental value for the energy of the normal helium atom.

5. Combination of §§1 and 2

The energy corresponding to the variation function $\Psi=a(1)a(2)+k(a(1)b(2)+b(1)a(2))$ is shown in curve C in Fig. 2 for the case that $Z=27/16$. The normalized function is $0.97a(1)a(2)+0.24(a(1)b(2)+b(1)a(2))$. It is not easy to minimize with respect to the effective charge so again the quadratic secular equation is solved for several values of the effective charge, the calculated energy being much higher when the effective charge is much different than 27/16. The lowest value obtained is $W=-5.805$ at $R=1.60a_0$, which, when subtracted from the value $-5.695W_H$ for the helium atom, gives a dissociation energy of $0.110W_H$ or 1.49 ev. The form of the variation function suggests that this is due to the partial formation of a covalent bond.

6. Combination of §§1, 2 and 3

The best variation function used is of the form $\Psi=a(1)a(2)+k_1(a'(1)a(2)+a(1)a'(2))+k_2(a(1)b(2)+b(1)a(2))$. On the basis of calculations 5 and 6, in which it was found that the best value of the effective charge was not far from 27/16, calculations were made only for the case that $Z=27/16$. The energy appears as a root of a cubic secular equation and is shown by curve D, Fig. 2 and by curve D, Fig. 1. The normalized function is $\Psi=0.97a(1)a(2)+0.10(a'(1)a(2)+a(1)a'(2))+0.20(a(1)b(2)+b(1)a(2))$. The lowest energy obtained is $-5.844W_H$ at $R=1.57a_0$. This, when subtracted from the helium atom value of $-5.695W_H$, gives a value for the dissociation energy of $0.149W_H$ or 2.02 ev. This dissociation energy is obtained by using the energy of the helium atom calculated from a variation function of the same type as the one used for the undissociated molecule. This pro-

cedure assumes that the error in the energy is the same at the equilibrium distance and at infinity. A lower limit for the dissociation energy is obtained by subtracting the minimum energy for the molecule from the experimental value, $-5.807W_H$, for the helium atom. The result is $0.037W_H$ or 0.50 ev. This positive result proves conclusively that the molecule is stable. The value 2.02 ev, however, is probably much closer to the actual value of the dissociation energy.

Fitting a parabola to the bottom part of the curve leads to a value for the force constant of 0.43 megadyne/cm and a fundamental vibration frequency of 2800 cm^{-1}.

The Molecule-Ion HeH^{++}

Doubly charged helium hydride molecule-ion was treated by the same type of variation function, $\Psi=a(1)+k_1b(1)+k_2a'(1)$. The resulting potential energy curve shows no minimum and differs only slightly from $-4W_H+e^2/R$. The one electron bond between the two atoms is not sufficiently strong to overcome the Coulomb repulsion. Another molecule in which there is Coulomb repulsion between the atoms, the helium molecule ion, He_2^{++}, has been treated by Pauling[7] including ionic terms in the variation function. In this case the electron pair bond formed is strong enough to overcome the Coulomb repulsion of the two atoms, there being a minimum in the potential energy curve. The instability of HeH^{++} is due to the lack of degeneracy of the two states He^+H^+ and $He^{++}H$.

Discussion

From a comparison of curves *B* and *C*, Fig. 2, it is seen that the introduction of polarization into the variation function is about half as effective in stabilizing the molecule as the introduction of the covalent bond. It is therefore qualitatively correct to say that two-thirds of the stabilization is due to the formation of a covalent bond and one-third is due to polarization of the helium atom. The strength of the bond, 2.02 ev, is surprisingly great in view of the small coefficients of the covalent bond term and the polarization term, 0.20 and 0.10, in the variation function given in section 6. It is roughly half as strong as the bond in the hydrogen molecule, 4.10 ev, calculated[6] from the same type of variation function.

I wish to thank Professor Linus Pauling for making many valuable suggestions during the preparation of this paper.

Appendix

The simpler integrals are omitted. The integrals, $M_{001,\,0}$ and $M_{010,\,0}$, are evaluated by the use of the Neumann expansion in confocal elliptic coordinates. The functions $H(m, n, \rho)$ and $S(m, n, \rho)$ are defined by Rosen.[5]

$$M_{000,\,0}=\int\frac{a^2(1)a(2)b(2)}{r_{12}}\,dv_1dv_2=\frac{Z}{a_0}\left\{e^{-\rho}\left(\frac{5}{16\rho}+\frac{1}{8}+\rho\right)-e^{-3\rho}\left(\frac{5}{16\rho}+\frac{1}{8}\right)\right\}$$

$$\begin{aligned}M_{001,\,0}=\int\frac{a^2(1)a'(2)b(2)}{r_{12}}\,dv_1dv_2=\frac{\rho}{2}\,M_{000,\,0}+\frac{Z}{a_0}\frac{\rho^6}{480}\,[A\{&-225H(5,4,\rho)+135H(5,2,\rho)+195H(3,4,\rho)-117H(3,2,\rho)\\&+225S(3,5,\rho)-60S(1,5,\rho)+225S(4,4,\rho)-120S(2,4,\rho)-195S(3,3,\rho)+72S(1,3,\rho)-135S(4,2,\rho)\\&+72S(2,2,\rho)\}+B\{375H(5,4,\rho)-225H(5,2,\rho)-195H(1,4,\rho)+117H(1,2,\rho)-375S(3,5,\rho)+100S(1,5,\rho)\\&-375S(4,4,\rho)-125S(2,4,\rho)+120S(0,4,\rho)+225S(4,2,\rho)+75S(2,2,\rho)-72S(0,2,\rho)+195S(3,1,\rho)\\&-72S(1,1,\rho)\}+C\{-375H(3,4,\rho)+225H(1,4,\rho)+225H(3,2,\rho)-135H(1,2,\rho)+375S(2,4,\rho)-100S(0,4,\rho)\\&+375S(3,3,\rho)-225S(3,1,\rho)-100S(1,3,\rho)-225S(2,2,\rho)+60S(0,2,\rho)+60S(1,1,\rho)\}]\end{aligned}$$

$$\begin{aligned}M_{010,\,0}=\int\frac{a(1)a'(1)a(2)b(2)}{r_{12}}\,dv_1dv_2=\frac{\rho}{2}\,M_{000,\,0}+\frac{Z}{a_0}\frac{\rho^6}{96}\,[A\{&9H(5,2,\rho)-3H(5,0,\rho)+9H(3,2,\rho)-3H(3,0,\rho)-9S(4,2,\rho)\\&+3S(4,0,\rho)-9S(1,5,\rho)+3S(2,0,\rho)\}+B\{-27H(5,2,\rho)+9H(5,0,\rho)-9H(1,2,\rho)+3H(1,0,\rho)\\&+27S(4,2,\rho)-9S(4,0,\rho)+9S(2,2,\rho)-3S(2,0,\rho)+27S(1,5,\rho)-3S(1,1,\rho)\}+C\{27H(3,2,\rho)-9H(3,0,\rho)\\&-9H(1,2,\rho)+3H(1,0,\rho)-27S(2,2,\rho)+9S(2,0,\rho)-27S(1,3,\rho)+9S(1,1,\rho)\}],\end{aligned}$$

where $$A=\int_{-1}^{+1}xe^{-\rho x}dx,\quad B=\int_{-1}^{+1}x^3e^{-\rho x}dx,\quad\text{and}\quad C=\int_{-1}^{+1}x^5e^{-\rho x}dx.$$

Dissociation of Excited Iodine Molecules

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By means of a sensitive optical method described elsewhere, we determined the quantum yield of the process

$$I_2+h\nu\rightarrow I+I$$

in mixtures of I_2 vapor with several hundreds of mms of He, A, H_2 and N_2, in three spectral regions: (1) In the continuum, i.e., on the short wave-length side of the convergency limit at 4990A; (2) in the band region immediately behind this limit, on its long wave-length side; and (3) in the band region further away from the limit. If the quantum yield is assumed to be $\gamma_1=1.00$ in the first region, the values $\gamma_2=1.14$ and $\gamma_3=1.10$ are obtained for the two other regions, showing *that all excited I_2 molecules dissociate by collisions with foreign molecules*. The quenching of I_2 fluorescence by foreign gases is thus practically never due to the dissipation process (1) $I_2^*+X\rightarrow I_2+X$ but entirely to the dissociation process (2) $I_2^*+X\rightarrow I+I+X$. The process (2) apparently occurs in most cases at the very first kinetic collision of excited iodine with a foreign molecule; only in the case of helium ten or more collisions are necessary to produce dissociation according to (2).

1. INTRODUCTION

WHEN a molecule of iodine vapor absorbs light of wave-length greater than 4990A, an excited I_2 molecule is produced, of which the natural mean lifetime is of the order of 10^{-7} sec. In sufficiently diluted vapor, the return into the normal state takes place under emission of fluorescence. The fluorescence is strongly quenched by an increase in the iodine pressure or by addition of a foreign gas. Two mechanisms of quenching are possible:

$$I_2^*+X\rightarrow I_2+X, \quad (1)$$

$$I_2^*+X\rightarrow I+I+X. \quad (2)$$

In the first case, the activation energy is dissipated in the form of kinetic, vibrational and rotational energy of the collision partners; in the second case it is mainly transformed into potential chemical energy of free iodine atoms. Quenching by dissociation is of course only possible if the activation energy is greater than the dissociation energy of the iodine molecule. This is, however, the case in the whole of the visible spectrum and even in the near infrared, up to 8200A. Some indirect arguments speak for the predominant part played by reaction (2):

(1) *The high efficiency of quenching*, as compared for instance with that observed in the resonance fluorescence of mercury vapor. This latter remains practically unaffected by nitrogen, helium or argon up to a pressure of several hundred millimeters. The intensity of iodine fluorescence is reduced to one-half its original value already by a few millimeters of nitrogen or argon and by something like 15–20 mm of helium. The electronic transition is of the same kind in both gases ($^3\Pi\rightarrow{}^1\Sigma$ in I_2, $^3P\rightarrow{}^1S$ in Hg). The probability of quenching by dissipation can therefore be supposed to be of the same order in both cases. It is reasonable to ascribe the strong quenching of I_2 fluorescence to the additional possibility of quenching by dissociation, which is impossible in the case of mercury. (Mercury fluorescence is strongly affected by hydrogen, probably due to the process $Hg^*+H_2\rightarrow Hg+H+H$, which is analogous to (2).)

(2) *Magnetic quenching.* I_2 fluorescence can be quenched by a magnetic field. In this case, no process of the kind (1) is possible, because of the lack of an acceptor for the activation energy. A process analogous to (2) is, however, possible, because the magnetic field can be substituted for the particle X in a "catalytical" dissociation of the excited I_2 molecule. This is in fact the explanation which was given to the magnetic effect by Turner[1] and Van Vleck.[2]

(3) From observations of the quantum yield of the *bromine*-hydrogen reaction Jost[3] concluded that the mechanism of this reaction is probably the same in the band region as in the continuous region of the bromine spectrum. It is therefore

[1] L. A. Turner, Zeits. f. Physik **65**, 464 (1930).
[2] J. H. Van Vleck, Phys. Rev. **40**, 544 (1932).
[3] W. Jost, Zeits. f. physik. Chemie **134**, 92 (1928); (B) **3**, 95 (1929).

probable that a great number of primarily excited Br_2 molecules dissociate into atoms by collisions with H_2 and Br_2 molecules. All these results together form a strong indirect evidence for the high probability of the reaction (2) and its preponderant role in the quenching of iodine fluorescence. The following experiments give a direct and quantitative proof of this assumption.

2. Experimental

In several previous papers[4, 5] we described a method of measuring the concentration of free atoms in strongly illuminated halogen vapors (or solutions). The method consists in observing the reversible decrease in the molecular extinction of the vapor which occurs when the absorption cell is exposed to intense illumination. The scheme of the apparatus is shown in Fig. 1. In discussing the results obtained with I_2 solutions in carbon tetrachloride and hexane[5] we mentioned that the quantum yield of dissociation of I_2 appears to be the same on both sides of the convergency limit at 4990A, thus indicating a dissociation of primarily excited I_2 molecules by collisions with the molecules of the solvent. The measurements in solution were, however, very rough indeed, because of the extreme smallness of the dissociation effect in a medium in which the recombination can occur at each collision of two iodine atoms.

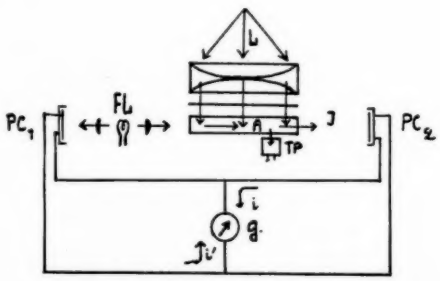

Fig. 1. L, parallel light beam from a 1500-watt automatic carbon arc; A, quartz vacuum cell (12×2×2 cm); TP, thermopile; FL, 6-v filament lamp; PC_1, PC_2, selenium-iron photo-cells, for measuring the light intensity I, and (after compensating the currents i and i') the intensity change ΔI occurring when A is illuminated by L; g, Zernicke galvanometer (Type Zc, sensitivity 1×10^{-10} amp. per mm).

We now repeated these experiments with iodine *vapor*. The dissociation effect is in this case large enough (of the order of 0.1 percent) to be exactly measurable by our optical arrangement, even when filtered light is used for illumination instead of the total light of the carbon arc. The most difficult task is not to measure the dissociation effect itself, but to determine with a sufficient accuracy the number of quanta absorbed per sec. in 1 cc of the vapor in each of the spectral regions used.

(a) *The spectral regions.* Fig. 2 shows the energy distribution in the three spectral regions which were used for the experiments. No. 1 lies completely in the continuous region of the I_2 spectrum, No. 2 in the band region close to the convergency limit, No. 3 in the same region further away from the limit. The energy distribution curves were obtained by means of a Hilger quartz double monochromator with a thermopile fixed behind its exit slit. (In the case of insufficient light intensity a selenium-iron photo-cell was substituted for the thermopile. Its spectral sensitivity was calibrated by comparison with the thermopile.) A certain difficulty is caused by the CN bands at 3860 and 4160A, the intensity of which varies even when the arc itself is burning quite steadily. An aesculin filter was used to decrease, as far as possible, the intensity especially of the 3860-band.

(b) *The mean extinction coefficients* $\bar{\alpha}$ were determined in two ways:

(A) By *calculation*, using the energy distribution curves given in Fig. 2, and the extinction curve of iodine vapor communicated by us in a previous paper.[5] The dotted curves in Fig. 2 show distribution of the light intensity *absorbed* by iodine in the three regions. The mean extinction coefficients are

$$\bar{\alpha} = \int \alpha_\lambda I_\lambda d\lambda / \int I_\lambda d\lambda. \qquad (3)$$

They were calculated by integrating graphically the curves given in Fig. 2.

(B) The values so obtained were checked *experimentally*, with a 6-v filament lamp as light source. It was impossible to use the carbon arc itself for exact measurements of $\bar{\alpha}$, because of its insufficient steadiness. In the regions No. 2 and

[4] E. Rabinowitch and H. L. Lehmann, Trans. Faraday Soc. **31**, 689 (1935).
[5] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32** (1936).

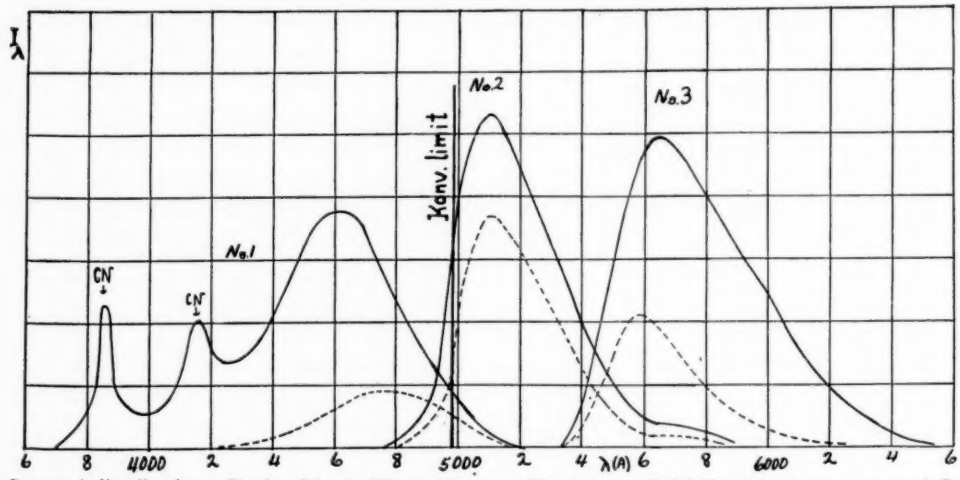

FIG. 2. Spectral distributions. Region No. 1: Filters Wratten No. 2 (aesculin)+No. 32+1 cm saturated $CuSO_4$ solution. Region No. 2: Jena glass GG11 (2 mm)+1 cm $Cu(NO_3)_2$ solution (2 vols. saturated solution, 1 vol. H_2O). Region No. 3: Wratten filter No. 21+11 mm $CuSO_4$ (1 vol. saturated sol., 1 vol. H_2O).

No. 3, the substitution of the filament lamp for the arc was permissible, as confirmed by the good agreement between calculated and experimental values of $\bar{\alpha}$ in Table I. In region No. 1, however, the energy distribution in the spectrum of the filament lamp is rather different from that in the arc spectrum, partially because of the difference in temperature, but more especially because of the absence of the CN bands in the lamp. We attempted therefore to measure $\bar{\alpha}$ for this particular region with the arc as light source as well. Single measurements gave strongly divergent results, because of the variations of the light intensity during the freezing out of the iodine vapor in the absorption cell. By averaging 40 single measurements, however, an $\bar{\alpha}$-value was obtained which was in good agreement with the calculated value (see Table I). Both values were 10 percent lower than the one obtained in experiments with the filament lamp. This difference can be accounted for by the CN bands, which increase the intensity of the arc in the region below 4300A, where the absorption by iodine becomes negligibly small.

TABLE I. *Mean extinction coefficients.*
$[\alpha=(760/pd)\log(I_0/I)]$

	Spectral Regions No. 1	No. 2	No. 3
1. Calculated	8.8	30.6	15.9
2. Observed with 6-v lamp (16°C)	9.8* 9.8**	29.8**	14.7**
(0°C)	9.5**	31.0**	15.0**
3. Observed with 25-amp. carbon arc	8.9*		

* Measured in vacuum.
** Measured in a helium atmosphere, $p=500$ mm.

In determining the "calculated" values of α, the "limiting" extinction curve[6] was used in the band region. This curve is obtained by using very low optical densities or by adding a sufficient amount of a foreign gas, in order to broaden the absorption lines of iodine so as to avoid an excessive absorption in the centers of the lines. The proof that these limiting conditions were realized in our experiments is given by the two sets of "experimental" values in Table I, obtained in a helium atmosphere ($p=500$ mm) with iodine vapor saturated at 16° ($p(I_2)=0.14$ mm) and 0° ($p(I_2)=0.030$ mm), respectively. Their identity shows the validity of Beer's law, which, in regions of band absorption can hold only under the "limiting" conditions.

In the following, the "calculated" values of $\bar{\alpha}$ (8.8; 30.6 and 15.9) were used as the most reliable ones.

(c) *The number of quanta absorbed* was determined by calculating the mean wave-length $\bar{\lambda}$ of the light absorbed by iodine in each of the three regions. Graphical integration was again used.

$$\bar{\lambda}=\int\lambda\alpha_\lambda I_\lambda d\lambda/\int\alpha_\lambda I_\lambda d\lambda. \qquad (4)$$

The values obtained in this way

$$\lambda=4720\text{A}\quad 5180\text{A}\quad 5660\text{A}$$

were only slightly different from the wavelengths corresponding to the *maxima* of the three absorption curves in Fig. 2 (4750, 5150 and 5580A). The total absorption of the illuminating light in the cell was only 0.8 percent in region No. 1, 2.8 percent in region No. 2, and 1.5 percent in region No. 3. The number of quanta $N_{h\nu}$ absorbed in 1 cc per sec. was therefore simply

$$N_{h\nu}=\text{const. } L\bar{\alpha}\bar{\lambda}, \tag{5}$$

where L means the intensity of the illuminating light (which was measured with a thermopile-galvanometer arrangement). The value of the constant in (5) is irrelevant, because we are concerned only with the comparison of the dissociation effects caused by the same number of absorbed quanta in the three spectral regions.

3. Calculation of Results

The change ΔI in the transmitted light intensity I (Fig. 1) caused by illumination L is proportional to the stationary decrease in concentration of I_2 molecules, i.e., to the concentration of I atoms in the illuminated gas. In experiments with Br_2 vapor[4] we made it plausible, that the recombination of free halogen atoms occurs in agreement with the kinetic rules derived theoretically for the elementary process

$$Br+Br+X\rightarrow Br_2+X. \tag{6}$$

We have been able since to prove this assumption by exact measurements with iodine, which results shall be published in a forthcoming paper. In order to obtain a practically pure homogeneous equilibrium:

$$I_2+h\nu\rightarrow I+I, \tag{7a}$$

$$I+I+X\rightarrow I_2+X, \tag{7b}$$

it is necessary to use pressures of X sufficiently high to prevent the walls from playing an appreciable role in the recombination.[6] We found that these conditions were realized under our geometrical conditions (and the light intensities used), at pressures above 150 mm with all gases except He and H_2, where pressures of the order of 400–500 mm are to be used. In the region of homogeneous equilibrium (7), the stationary concentration of iodine atoms is proportional to the *square root* of their rate of production. This rate is:

$$+d[I]/dt=2\gamma N_{h\nu}, \tag{8}$$

where γ is the quantum yield of dissociation. Therefore:

$$2\gamma N_{h\nu}=\text{const. } (\Delta I)^2, \tag{9}$$

or on account of (5)

$$\gamma=\text{const. } (\Delta I)^2/L\bar{\alpha}\bar{\lambda}. \tag{10}$$

Our purpose is to compare the rate of production of atoms in region No. 2 (and No. 3) to that in region No. 1, where the quantum yield is surely $\gamma_1=1$. According to (10) the quantum yield is:

$$\gamma_2=((\Delta I)_2^2/(\Delta I)_1^2)(L_1\bar{\alpha}_1\bar{\lambda}_1/L_2\bar{\alpha}_2\bar{\lambda}_2). \tag{11}$$

A corresponding equation holds for γ_3.

In Table II, results are given of experiments with helium, hydrogen, argon and nitrogen as foreign gases, added to 0.14 mm of iodine vapor. The last two columns show the values of γ_2 and γ_3 obtained in different gases.

TABLE II. *Dissociation effect in different spectral regions* $p(I_2)=0.14$ *mm.*

	No. 1 $\bar{\lambda}=4720$ $\bar{\alpha}=8.8$			No. 2 $\bar{\lambda}=5180$ $\bar{\alpha}=30.6$			No. 3 $\bar{\lambda}=5660$ $\bar{\alpha}=15.9$				
X p_X	L	$L\bar{\alpha}\bar{\lambda}$	ΔI	L	$L\bar{\alpha}\bar{\lambda}$	ΔI	L	$L\bar{\alpha}\bar{\lambda}$	ΔI	γ_2	γ_3
He 525	7.46	3.10	10.5	2.75	4.36	13.1	5.40	4.86	13.9	1.11	1.14
A 340	8.9	3.70	7.8	2.40	3.8	8.3	4.8	4.32	8.9	1.11	1.11
A 220	8.33	3.47	8.8				5.4	4.0	9.9		0.90
H_2 386	15.1	6.28	7.8	3.00	6.9	7.2	10.9	9.8	10.8	1.13	1.25
N_2 184	12.1	5.03	10.7	4.37	6.9	14.3	13.1	11.8	17.4	1.24	1.12

The magnitude of the dissociation effect observed in these experiments (which we mention for orientation, although it is irrelevant for the calculation of γ) is given by:

$$\frac{\Delta I}{I}=\frac{\Delta[I_2]}{[I_2]}\bar{\alpha}_I\frac{p}{760}d\ln 10.$$

The values involved were $\bar{\alpha}_I$ (extinction coefficient for the photo-cell light I) $=20$; p (pressure of iodine) $=0.14$; d (length of the cell) $=12$ cm. The relative changes of the light intensity $\Delta I/I$ were of the order of 2×10^{-4}. This means

$$\frac{\Delta[I_2]}{[I_2]}=\frac{2\times10^{-4}\times760}{20\times0.14\times12\times2.3}\backsimeq0.002.$$

About 0.2 percent of the I_2 molecules were thus dissociated into atoms in the stationary state during illumination.

[6] It is of course possible to work in the region of mixed homogeneous-heterogeneous recombination as well, but in this case the light intensities must be adjusted so as to give exactly the same numbers of quanta absorbed in all the three spectral regions, because under these conditions ΔI is an unknown function of L (between const.$\times L$ and const.$\times L^{\frac{1}{2}}$).

The values of γ_1, and γ_2 shown in Table II, are all equal to 1 within the limits of the experimental error. We may thus conclude, that *beginning from the convergency limit at 4990A and up to the red limit of region No. 3, i.e., up to 6200A, practically every excited I_2 molecule dissociates into atoms by collisions with molecules of helium, argon, nitrogen or hydrogen.*

The quenching of iodine fluorescence by all these gases is thus entirely due to the dissociation reaction (2). The velocity of (2) is therefore equal to that of the quenching process. The quenching curves, measured by Franck and Wood[7] and more recently by Berg and Rössler[8] show that in case of all gases except helium the quenching occurs at the very first (or one of the first few) kinetic collisions. This is shown by the following calculation: The quenching constants for A, N_2 and O_2 are, according to Berg, of the order of 1.5–2. These are the constants of the Stern-Volmer equation $I_x = I_0/(1+\text{const.}\times p_x)$, I_0 measuring the intensity of fluorescence without quenching, I_x that in presence of p_x mm of the gas X. (The value of I_0 must be extrapolated to $p(I_2)=0$ in order to account for the self-quenching by iodine.) These values of the constants mean that $I_x = I_0/2$ at $p_x \backsimeq$ *ca.* 0.7 mm $= 7\times10^{-3}$ atmos. The fluorescence is reduced to 1/2 its original value when the mean time between excitation and emission is equal to the mean time between excitation and quenching. The first being about 10^{-7} sec.[9] in the case of I_2 ($^3\Pi_0$), the second must be of the same order as well. The mean kinetic collision-interval is 10^{-10} sec. at 1 atmos.; and 10^{-7} at 0.001 atmos., and is thus identical with the mean "quenching time." The I_2* molecules are thus unable to stand gas-kinetic collisions with A, N_2 or O_2 without dissociation. They are somewhat stabler against collisions with helium molecules. A He pressure of 20 mm is needed for reducing the intensity of fluorescence by 50 percent in green and something of the order of 70 mm to reduce it by the same amount in the red. In our experiments at 500 mm helium no trace of fluorescence was recognizable and the dissociation even in the long wave region No. 3 was as complete in helium as in all other gases.

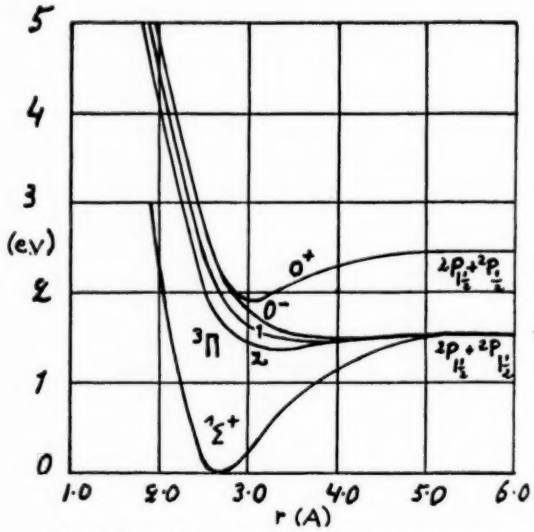

FIG. 3. Potential curves of the iodine molecule.

The mechanism of the secondary dissociation of excited I_2* molecules is probably the one indicated by Turner,[2] and theoretically elucidated by Van Vleck.[3] It is illustrated by Fig. 3, taken from Van Vleck's paper. The transition from the "stable" excited state $^3\Pi_{0^+}$ to the unstable repulsive state $^3\Pi_{0^-}$ is prohibited in a free iodine molecule; the symmetries which make it impossible are, however, destroyed by a magnetic or an inhomogeneous electric field. The activated molecules I_2* dissociate therefore under the influence of a magnetic field or of the inhomogeneous molecular fields which act on them during the collisions. The transition becomes more difficult when the potential curves $^3\Pi_{0^+}$ and $^3\Pi_{0^-}$ are more widely separated,—this is why the fluorescence is less sensitive in the red than in the green region.

At the end, we wish to express our heartiest thanks to Professor F. G. Donnan for giving us the opportunity of working in the Sir William Ramsay Laboratories and for his interest and invaluable support during the work.

[7] J. Franck and R. W. Wood, Verh. d. D. phys. Ges. **13**, 78 (1911).

[8] W. Berg, Zeits. f. Physik **79**, 89 (1933); F. Rössler, Zeits. f. Physik **96**, 251 (1935).

[9] We think that the lifetime of $I_2(^3\Pi_0)$ must be nearer 10^{-7} than 10^{-8} sec. because of the analogy with the $^3P_1$ state of Hg, whose lifetime is well known to be 10^{-7} sec.

Free Energy and the Rate of Chemical Reactions

The Relation Between the Rate and Oxidation-Reduction Potentials

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The theories of the rates of chemical reactions previously developed by Eyring, Rice and the author give a relationship between the rate of reaction and the free energy of formation of the activated state. With the aid of this relation it is possible to explain the experimental data which have shown that there is a connection between the rates of oxidation-reduction reactions and the potentials of the reagents used.

I. INTRODUCTION

SOME years ago, Conant and his co-workers[1] pointed out that there was a definite relationship between the rate of an irreversible oxidation-reduction reaction and the oxidation-reduction potentials of the reagents that are used. With the aid of some assumptions concerning the mechanism of such reactions, they were able to derive an equation relating the relative rates of reaction with two different reagents with the normal potentials of these reagents. It was found that the agreement with experimental data was satisfactory. The studies of Conant and his collaborators have been continued and extended by Chow,[2] who also has found that a relationship between oxidation reduction potentials and the rates of some reactions can be expressed by a simple empirical equation. This work has made it evident that there exists some connection between the kinetic rate constant and thermodynamic quantities. Such a conclusion is also indicated by the data in the fields of acid and basic catalysis.

Until quite recently, there seemed to be no theoretical justification of the existence of such relationships. The collision theory of the rates of chemical reactions had no connection with thermodynamics. Within the past year, however, Eyring, Rice and the author[3] have developed theories of the absolute rates of chemical reactions which serve to relate the data of kinetics with thermodynamic quantities. O. K. Rice and the author have shown how one may determine the absolute rates of unimolecular decompositions and bimolecular associations from the entropy change involved in the reactions. Wynne-Jones and Eyring[4] have related the abnormal rates of some reactions in solution to the entropy of formation of an "activated complex." The rate can also be simply related to the free energy change involved in the formation of an activated state. Since the free energy change and the e.m.f. are directly proportional, it is possible to obtain a theoretical derivation of a relation between the rate of a reaction and the oxidation-reduction potentials of the reagents involved. In the following, we shall borrow freely from the notation and terminology of Eyring and his co-workers as well as those of Rice and the author, in accordance with the method used in reference 3c.

II. THE RELATION BETWEEN THE SPECIFIC RATE CONSTANT AND OXIDATION-REDUCTION POTENTIALS

It has been shown that the rate of a chemical reaction is given by the concentration of the reacting systems in a certain fraction of the total phase space that is available to the systems, multiplied by the velocity with which the systems are passing through this region.[3] The configuration of the reacting molecules which corresponds to this region of phase space may be called the activated complex. That is, if one wishes to describe the particles in the systems by

[1] Conant, Chem. Rev. **3**, 1 (1926); Conant and Pratt, J. Am. Chem. Soc. **48**, 3178, 3220 (1926), and earlier papers.

[2] Chow and Kammerling, J. Biol. Chem. **104**, 69 (1934); Chow, J. Am. Chem. Soc. **56**, 894 (1934); ibid. **57**, 1437, 1440 (1935).

[3] (a) Eyring, J. Chem. Phys. **3**, 307 (1935); (b) O. K. Rice and H. Gershinowitz, ibid. **2**, 857 (1934) and (c) ibid. **3**, 479 (1935).

[4] (a) Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935); see also (b) Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935).

means of their coordinates and momenta, the concept of position in phase space is used. If one prefers to describe the particles by means of their coordinates and potential energies, one speaks of the activated complex. It has been shown that the two methods give the same results. The velocity of these systems or activated complexes, expressed in units of cells of phase space of size h per second, is kT/h, where T is the absolute temperature and k and h are the Boltzmann and Planck constants, respectively. If (C) is the concentration of activated complexes per unit length h, the specific rate of any reaction is given by

$$k_1=(C)kT/h=(C)\cdot v, \tag{1}$$

where we write v for kT/h in order to simplify the writing of subsequent equations.

Now if we represent the equilibrium reaction by which the activated complex is formed as

$$nA+mB\rightleftarrows C \tag{2}$$

the equilibrium constant for the reaction is

$$K=(C)/(A)^n(B)^m. \tag{3}$$

At unit concentration of reactants $K=(C)$ and the specific rate constant becomes[4]

$$k_1=K\cdot v. \tag{4}$$

From thermodynamics we get the relation

$$\ln K=-\Delta F^*/RT, \tag{5}$$

where ΔF^* is the free energy of formation of the activated state. Substituting for K in (4),[5]

$$k_1=\exp(-\Delta F^*/RT)\cdot v. \tag{6}$$

In general, ΔF^* is not the same as ΔF, the free energy change for the total reaction. The calculations of the absolute rates of unimolecular decompositions and bimolecular associations in the gas phase[3b, c] indicated that the entropy change for the formation of the activated state is, in most cases, equal to zero for the decompositions and equal to the entropy change for the total reaction in the case of the associations, i.e., the activated state has approximately the same entropy as the normal associated molecule. The calculations of Wynne-Jones and Eyring[4] show that for many reactions in solution, also, the entropy change for the formation of the activated complex is equal to the total entropy change in the reaction. For the free energy change in such reactions to be equal to the free energy of formation of the activated complex, it would be necessary that the energy of formation of the activated state be equal to the energy of the reaction. This will be so only if the energy of activation of the reverse reaction is zero, since the energy change for the reaction is equal to the difference of the activation energies of the forward and reverse reactions.[6] We see, therefore, that the free energy of formation of the activated state will rarely be equal to the free energy change for the total reaction.[7] It is this fact that has obscured the relation between free energy and the rate of reaction.

For a reversible reaction, we have the relation

$$\Delta F^*=-n\mathrm{F}E^*, \tag{7}$$

where n is the number of equivalents, F the Faraday and E^* the e.m.f. for the reaction by which the activated complex is formed. Substituting (7) in (6) we have, finally,

$$k_1=\exp(n\mathrm{F}E^*/RT)\cdot v. \tag{8}$$

With Eq. (8) as a basis, we can now determine the relation between the potential of a reagent and the rate of a reaction. For organic oxidations, Conant and Pratt proposed the following mechanism

$$\begin{aligned}&\mathrm{ROH}+\mathrm{B}\rightleftarrows\mathrm{RO}^-+\mathrm{BH}\\ &\mathrm{RO}^-\rightarrow\mathrm{R}=0.\end{aligned} \tag{9}$$

This type of reaction can readily be treated by the theoretical method that we have just proposed. An added advantage of such a treatment is that, in order to obtain relative rates, it is not necessary to assume as particular a mechanism

[5] A similar relation between the free energy and the reaction rate has been obtained by V. K. La Mer (J. Chem. Phys. **1**, 291 (1933), Eq. (10) et seq.), by means of thermodynamic analogies from Tolman's general expression for the temperature coefficient of the rate of reaction. The most important difference lies in the fact that in the expression we have derived there is no arbitrary constant, since we have obtained directly the integrated form of the expression for the specific rate constant so that there is no question of an undetermined constant of integration.

[6] Gershinowitz and Rice, J. Chem. Phys. **2**, 273 (1934).

[7] There does seem to be at least one reaction for which the free energy change that determines the rate of the reaction is the same as the total change in free energy. This is the autoxidation of hydroquinone, catalyzed by manganous salts in acid solutions, studied by La Mer and Temple (Proc. Nat. Acad. Sci. **15**, 191 (1929)).

as that which Conant and Pratt used to explain the relation between e.m.f. and the rate of reaction. If one does however, postulate a definite mechanism, it becomes possible to calculate not only the relative rates, but also the absolute values of the rate constants. It is also possible to extend the theoretical equations to include the more complex systems studied by Chow.

Let us assume that we have a substance A which is to be oxidized by some reagent B, and that the activated complex C consists of some oxidized form of A, say A', and B', the reduced form of B. At this point it is not necessary to know the further mechanism of the reaction, or whether the oxidized form of the molecules A is a single molecule or a polymolecular complex. All that we need know is that the rate determining step for the reaction is the passing of this complex through a certain region of phase space, no matter whether the motion represents a unimolecular rearrangement or some bimolecular or polymolecular change. The change in potential involved in the formation of the activated state is

$$E^* = E_{A'} - E_A + E_{B'} - E_B. \qquad (10a)$$

At unit concentration of reactants

$$E_{B'} - E_B = E_{0B}, \qquad (10b)$$

where E_{0B} is the normal oxidation-reduction potential of B. Hence, from Eq. (7),

$$k_1 = \exp\,(n\mathrm{F}(E_{A'} - E_A + E_{0B})/RT)\cdot\nu. \qquad (11)$$

If instead of B, we used some other oxidizing agent D, the rate would be given by

$$k_1' = \exp\,(m\mathrm{F}(E_{A'} - E_A + E_{0D})/RT)\cdot\nu. \qquad (12)$$

If $n = m$,

$$k_1/k_1' = \exp\,[(E_{0B} - E_{0D})n\mathrm{F}/RT] \qquad (13a)$$

or

$$\ln\,(k_1/k_1') = [E_{0B} - E_{0D}]\cdot n\mathrm{F}/RT. \qquad (13b)$$

By substituting numerical values for the universal constants, and letting $n = 2$, as in some cases studied by Conant and Pratt,

$$0.03\,\log\,(k_1/k_1') = E_{0B} - E_{0D}. \qquad (14)$$

This equation is identical with Eq. (11) of Conant and Pratt, which was found to give satisfactory agreement with the experimental data. We see that this relationship is a direct consequence of the new theories of the absolute rate of chemical reactions, and that it may be derived without assuming the unimolecular mechanism that Conant *et al.* found it necessary to use.

An essential distinction between the method we have used and that employed by Conant and his co-workers is involved in the nature of the equilibrium processes. Conant and Pratt,[8] for example, assume the following mechanism for the reduction of an azo dye,

$$\mathrm{RN{=}NR'OH + BH_2 \rightleftarrows RNHNHR'OH + B}$$

$$\mathrm{RNHNHR'OH \xrightarrow[\text{slow}]{} RNH_2 + R'(=O)(=NH)}.$$

The second of these reactions is the one that may be considered to go through an activated complex. But according to the method that we have used, it does not matter how many intermediate steps there are between this step and the initial reactants. As long as the activated complex is the same, the rate of the reaction will depend only on the potential of the reducing agent. Rice[9] has made clear the distinction between flux equilibrium and "back and forth" equilibrium. In the theory of the activated complex the complex is in flux equilibrium with the normal reactants. This is why an apparently equilibrium method can give information about rates of reactions that are not in equilibrium. It is the free energy of the state of the system that is in flux equilibrium that determines the rate of the reaction. All the intermediate configurations that are in "back and forth" equilibrium will drop out of the calculation. It is thus clear that the method of the activated complex is more complete and rigorous than that used by Conant, which is a special case, and that it will explain all the data that the latter will. This explicit definition of the nature of the activated complex also distinguishes this treatment from that based on the Bronsted-Bjerrum type of complex, which is not rigorously defined.

Chow has found that it is possible to explain

[8] Conant and Pratt, J. Am. Chem. Soc. **48**, 2464 (1926).
[9] O. K. Rice, J. Phys. Chem. **4**, 53 (1936).

the experimental data for the kinetics of various oxidation-reduction reactions by means of a simple empirical relationship which he has proposed, namely

$$\text{rate} \propto \exp(nFE/3RT). \qquad (15)$$

Using this equation, he has obtained good agreement with the data on the catalytic absorption of oxygen by linseed oil, and the oxidation of formate and oxalate ions by halogens in the dark. While the general form of this relation is that which would be expected from Eq. (8), it seems rather difficult to construct a mechanism for the formation of the activated complex which would give the exact dependence on the potential that is given by Chow. It is possible to construct several mechanisms that give the relation, rate $\propto \exp(nFE/2RT)$, but while these give good constants within a run, they do not give good results from run to run. From the data it would seem that a dependence on $(nFE/3RT)$ is actually demanded. Such a relation can be obtained from a mechanism which demands the formation of a complex from three equivalents of the reagent. It would seem that more data are needed to help decide what is the nature of the activated complex. A step in this direction is afforded by the recent work of Abel and Schmid,[10] who have obtained indirect spectroscopic evidence of the presence of the ion $[CO_2CO_2^-]$ in the oxidation of oxalate ion by iodine.

III. Discussion

Bancroft and Magoffin[11] have recently discussed the role played by excited energy levels in electrochemical processes. The method which they have used may be correlated with that of Conant by means of the approach used above. They state that the concept of an intermediate energy level which they use is quite different from the assumptions of a reversible electrolytic process and a practically irreversible nonelectrolytic one made by Conant and his collaborators. From the treatment we have given, however, it may be seen that both methods are essentially the same, being qualitative descriptions, in different words, of the fact that the rate of reaction is determined by the concentration of an intermediate configuration of the system, which is in equilibrium with the reactants.

The development of rigorous thermodynamics and the kinetic theory explanation of the rates of chemical reactions served to discredit the idea, prevalent since the time of van't Hoff, that the rate of a reaction should be determined by the free energy change. The theories of reactions recently developed, which take into account all the degrees of freedom of the reacting molecules, especially in the form developed by Eyring, which makes explicit use of an activated complex, show that the rate of a reaction is determined by a free energy change, which is usually not the same as the free energy change for the total reaction. The theory of Bronsted and Bjerrum, which introduced an intermediate complex, explained some of the relationships between rates and quantities usually associated with equilibrium measurements. La Mer has shown the relation between the free energy change and the concept of the critical complex.[5] In these treatments, however, there still remained arbitrary constants. Wynne-Jones and Eyring and Evans and Polanyi[4] have shown quantitatively the relation between the theory of Bronsted and Bjerrum and the general theory of the activated complex which applies to gas phase reactions, as well as to reactions in solution. The regularities observed for oxidation-reduction reactions and for acid and basic catalysis should no longer be considered as isolated phenomena, but as being manifestations of the existence of some critical configuration of the reactants. This relation between the two types of reaction helps to explain why Abel and Hilferding[12] were able to describe formally the reaction between oxalate ion and iodide ion as either an oxidation-reduction reaction or a reaction catalyzed by H^+. Also, as Bancroft and Magoffin have remarked, there is no need to make any fundamental distinction between hydrogenation and reduction. It should now be possible to treat all reactions, homogeneous or heterogeneous, by the same theoretical methods.

[10] Abel and Schmid, Naturwiss. **23**, 501 (1935).
[11] Bancroft and Magoffin, J. Am. Chem. Soc. **57**, 2561 (1935).
[12] Abel and Hilferding, Zeits. f. physik. Chemie **A172**, 353 (1935).

On the Thermodynamic Properties of Nitric Oxide An Example of an Associated Liquid

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Liquid nitric oxide consists largely of double molecules, as evidenced by the abnormally high entropy of vaporization and the high and variable specific heat. By making use of these data it is possible to calculate the extent to which single molecules exist in the liquid, the heat of dissociation of the double molecules, and the value the specific heat would have were the association in the liquid complete. A statistical calculation is made of the entropy of vaporization, and the result compared with the experimental value. An estimate is made of the heat of dissociation in the gas phase.

§1.

THE existence of associated nitric oxide molecules has been inferred from the equation of state[1] and from the abnormally high heat and entropy of vaporization,[2] and Johnston and Weimer have remarked that the abnormally high and rapidly varying specific heat of the liquid indicates the beginning of dissociation of the double molecules near the boiling point.[3] But though Eucken and d'Or[1] did attempt to make some estimate of the degree of association in the gas and the dissociation energy of the double molecules, the full possibilities of the available data have not, so far as I am aware, been realized.

Let us first consider the entropy of vaporization,[4] $\Delta_v S$. As we have stated, this is considerably higher than it would be were nitric oxide a normal unassociated liquid. The entropy of vaporization of this hypothetical normal liquid, which may be estimated by means of Hildebrand's rule or by a comparison with normal liquids which boil around the same temperature, we shall call[4] $\Delta_H S$. This is the entropy of vaporization of the ideal normal liquid to give vapor at the vapor pressure of the actual liquid, e.g., at one atmosphere if the temperature is the observed boiling point. Let N be Avogadro's number, N_1 the number of $(NO)_2$ molecules, and N_2 the number of NO molecules in one mole of nitric oxide. We shall assume that NO and $(NO)_2$ form a perfect solution, so that the vapor pressure P_H of the unassociated liquid bears to the actual vapor pressure, P_v, the ratio* $(N_1+N_2)/N_2$. This characterization of the perfect solution includes the assumption that the vapor is a perfect gas. It may appear that this is not always justified, for at the boiling point of nitric oxide P_H may be expected to be several atmospheres. All difficulties are avoided, however, if by P_H and P_v we understand the hypothetical vapor pressures which would obtain if the vapor were a perfect gas, and if all heats of evaporation are taken to be the heats for the formation of such a perfect vapor. The only error which will then occur is that arising from the assumption, which we shall make when we use the observed heat of evaporation, that the real vapor is a perfect gas at *one* atmosphere and that it is completely dissociated. This error is negligible.

Now the heat of evaporation of the actual liquid,[4] $\Delta_v H$, is related to the heat of evaporation,[4] $\Delta_H H$, of the normal liquid, by the equation

$$\Delta_v H=\Delta_H H+(N_1/N)\Delta H, \qquad (1)$$

where ΔH is the change of heat content on dissociation per mole of $(NO)_2$. Hence

$$\Delta_v S=\Delta_H H/T+(N_1/N)\Delta H/T. \qquad (2)$$

But $\Delta_H H/T$ is the entropy of vaporization of the normal liquid to vapor at its equilibrium pressure, P_H; to get $\Delta_H S$ we must add the change of entropy when the pressure is reduced to P_v. Thus, since $P_H/P_v=(N_1+N_2)/N_2$,

[1] Eucken and d'Or, Nachrichten Gesell. Wiss. Göttingen, Math.-phys. Klasse (1932), p. 107. See also Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 170.

[2] See e.g., Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929), especially pp. 3208, 3213.

[3] Johnston and Weimer, J. Am. Chem. Soc. **56**, 625 (1934). See footnote 19.

[4] This quantity is referred to unit amount (one mole) of nitric oxide (NO) whether single or combined with another NO to form a double molecule.

* See Hildebrand, *Solubility*, 2d Ed., p. 19. (We assume the vapor pressure of the *associated* liquid to be zero.)

$$\Delta_H S = \Delta_H H/T + R \ln [(N_1+N_2)/N_2]. \quad (3)$$

From (2) and (3)

$$R \ln [N_2/(N_1+N_2)] = \Delta_v S - \Delta_H S - (N_1/N)\Delta H/T. \quad (4)$$

Now the change of P_v with the temperature will be given approximately by the Clausius-Clapeyron equation $Rd \ln P_v/dT = \Delta_v H/T^2$ and similarly $Rd \ln P_H/dT = \Delta_H H/T^2$, so that

$$Rd \ln (P_v/P_H)/dT = Rd \ln [N_2/(N_1+N_2)]/dT = \Delta_v H/T^2 - \Delta_H H/T^2 = (N_1/N)\Delta H/T^2. \quad (5)$$

Eq. (4) is an integrated form of Eq. (5).

Let us now see what information may be gleaned from the specific heat data. If we assume that the excess specific heat,[4] $C_p' = C_p - C_{p,0}$, where C_p is the observed specific heat[4] and $C_{p,0}$ is the specific heat of the hypothetical completely associated liquid,[4] we have

$$C_p' = (dN_2/dT)(\Delta H/2N). \quad (6)$$

Now from (5) we have

$$d[N_2/(N_1+N_2)]/dT = [N_2/(N_1+N_2)](N_1/N)\Delta H/RT^2,$$

which yields, remembering $2N_1+N_2=N=$ constant,

$$\frac{dN_2}{dT} = \frac{2(N_1+N_2)N_1N_2}{N^2}\frac{\Delta H}{RT^2}. \quad (7)$$

Now since N_1/N and $(N_1+N_2)/N$ are both almost exactly equal to† $\frac{1}{2}$ and since one of them is less than $\frac{1}{2}$ by the same amount that the other exceeds it we can safely set $dN_2/dT = N_2\Delta H/2RT^2$, which yields, assuming ΔH constant,

$$N_2 = b \exp(-\Delta H/2RT), \quad (8)$$

where b is a constant. Since C_p' is proportional to dN_2/dT and hence to N_2/T^2 we see from (8) that

$$C_p' = aT^{-2} \exp(-\Delta H/2RT), \quad (9)$$

where a is a constant. We may write (9) in the form

$$C_p' = a' \exp[-(\Delta H - 4RT_b)/2RT], \quad (10)$$

T_b being the value of T at the boiling point. $a' = aT^{-2} \exp(-2T_b/T)$, which may for purposes of approximation be regarded as constant. If we plot log C_p' against $1/T$ we should thus get a straight line, from the slope of which ΔH may be calculated (still assuming it is independent of temperature). Experimentally, however, we have C_p, not C_p'. In order to obtain C_p', therefore, we need to know the value of $C_{p,0}$. We have tried calculating C_p' by setting $C_{p,0}$ equal to arbitrary values, 10, 11, and 12 calories per degree per mole of nitric oxide. This neglects the fact that $C_{p,0}$ may not be exactly constant, and also the fact that the specific heat of a mixture of double and single molecules (as exists after some of the latter have been formed) is slightly different from that of the pure associated liquid, even forgetting the heat absorption due to further dissociation. In all cases a fairly good straight line is obtained by plotting log C_p' against $1/T$. In Table I we have listed the values of ΔH corresponding to the various assigned values of $C_{p,0}$.

It is now possible finally to determine ΔH by integrating Eq. (6). We get

$$(2/\Delta H)\int_0^{T_b} C_p' dT = (N_2/N)_b, \quad (11)$$

(The subscript b indicates that a quantity is to be evaluated at the boiling point.) From Eqs. (9) and (11) we have

$$(N_2/N)_b = (2a/\Delta H)\int_0^{T_b} T^{-2} \exp(-\Delta H/2RT)dT = 4Ra(\Delta H)^{-2} \exp(-\Delta H/2RT_b) = 4RT_b^2 C'_{p,b}(\Delta H)^{-2}. \quad (12)$$

We can thus determine the value of $(N_2/N)_b$ that corresponds to any given value of ΔH. This is also given in Table I. We can now substitute $(N_2/N)_b$ back into Eq. (4) and determine the value of ΔH given by that equation (after evaluating $\Delta_v S - \Delta_H S$ as discussed in the next paragraph). The values of ΔH thus determined are likewise given in Table I. Now in order for the calculation to be self-consistent the two values of ΔH must coincide. This occurs if $C_{p,0} = 11.1$, $(N_2/N)_b = 0.062$, and $\Delta H = 3910$.

TABLE I. (Energy units, calories per mole.)

$C_{p,0}$	ΔH, Eq. (10)	$(N_2/N)_b$	ΔH, Eq. (4)
10	3390	0.092	3840
11	3840	0.064	3900
12	4440	0.042	4010

† Since the liquid is almost completely associated, according to assumption, which turns out to be consistent with the results subsequently obtained.

The entropy values in Eq. (4) are obtained as follows. $\Delta_v S$ is known from the work of Johnston and Giauque[2] to be 27.13 entropy units per mole of nitric oxide. $\Delta_H S$ is estimated on the assumption that the normal unassociated nitric oxide would be like oxygen, which boils at 90.1°K with an entropy of vaporization of 18.1 entropy units.[5] Assuming that the difference between the specific heats of the unassociated nitric oxide gas and liquid is the same as for oxygen, about 6 calories per mole per degree, we calculate that at the boiling point of nitric oxide $\Delta_H S = 16.3$ entropy units. The chief source of error in our results is presumably the uncertainty in $\Delta_H S$, which might well be incorrect by one entropy unit, or possibly even somewhat more. An error of one entropy unit would cause an error of 300 calories in the value of ΔH.

§2.

It will now be of interest to attempt to compare the value assigned to $\Delta_v S - \Delta_H S$ with the value which may be obtained theoretically with the aid of statistical mechanics and reasonable assumptions as to the properties of the associated molecules. Let us consider the entropy of a mixture of NO and $(NO)_2$ molecules contained in a volume V. If we assume that there are no forces between the molecules the total entropy[4] may be written in the form[6]

$$S = N_1 S_1 + N_2 S_2 + k \ln (N!/N_1!N_2!), \quad (13)$$

where S_1 and S_2 are quantities which may be called the entropies per molecule of $(NO)_2$ and NO, respectively, and k is the Boltzmann constant, R/N. The last term in (13) is the entropy contribution due to the possibility of having different individual NO's combined in the $(NO)_2$ molecules.

The entropies S_i ($i=1$ or 2) may be written in the form

$$S_i = k \ln (VB_i C_i D_i E_i) = S_i^\circ + k \ln V, \quad (14)$$

where VB_i, C_i, and E_i are the contributions due, respectively, to the translation, the rotation, and the vibration of the molecule, and D_i is that due to electronic degeneracy, etc. We have

$$B_i = (2\pi e m_i kT/h^2)^{3/2}, \quad (15)$$

where e is the base of natural logarithms, m_i is the mass of the molecule, and h Planck's constant;

$$C_i = C_{i'} C_{i''} \cdots, \quad (16a)$$

with

$$C_{i'} = \pi^{-1}(8\pi^3 e I_{i'} kT/h^2 \sigma_{i'}^2)^{l_{i'}/2},$$

$$C_{i''} = (8\pi^3 e I_{i''} kT/h^2 \sigma_{i''}^2)^{l_{i''}/2}. \quad (16b)$$

. . . . . .

where $C_{i'}$, $C_{i''}$, $\cdots$ refer to different types of rotation, involving, respectively, $l_{i'}$, $l_{i''}$, $\cdots$ degrees of freedom, and having moments of inertia $I_{i'}$, $I_{i''}$, $\cdots$ $(I_{i'} > I_{i''} > \cdots)$ and symmetry numbers $\sigma_{i'}$, $\sigma_{i''}$, $\cdots$; and E_i is a complicated but well-known function of the quantities $h\nu_{ij}/kT$, where the ν_{ij} are the frequencies of the molecule.

Eq. (13) applies to a dilute gas; it may also be applied to a liquid, provided the forces are of such a nature that they can be taken into account by assigning to V a certain effective value, not equal to the actual volume of the liquid, but in general much smaller, since a molecule cannot occupy the space already occupied by another molecule. This assumption, together with the assumption that V is proportional to N_1+N_2, is equivalent to the assumption that NO and $(NO)_2$ form a perfect solution, as we shall see.

We consider the entropy change in the process whereby the liquid changes from a completely unassociated one with $N_1=0$, $N_2=N$, and $V=V_H$ to the actual liquid with $N_1=N_1$, $N_2=N_2$, and $V=V$. By Eq. (13) this entropy change will be (using Stirling's approximation for factorials)

$$\Delta_0 S = N_1 S_1^0 + N_2 S_2^0 - N S_2^0 - Nk \ln V_H + (N_1+N_2)k \ln V + Nk \ln N - N_1 k \ln N_1 - N_2 k \ln N_2 + (N_1+N_2-N)k,$$

where the S_i^0 are defined in Eq. (14). Remembering now the relation between V and V_H (the effective volume being proportional to N_1+N_2) and that $2N_1+N_2=N$ this reduces to

$$\Delta_0 S = N_1 \Delta S^0 - (N_1/N)R \ln V + R \ln (N_1+N_2) - (N_1/N)R \ln N_1 - (N_2/N)R \ln N_2 - (N_1/N)R, \quad (17)$$

where $\Delta S^0 = S_1^0 - 2S_2^0$. Now the equilibrium constant is given by

$$\ln K = \ln (N_1 V/N_2^2) = \Delta S^0/k + \Delta E/RT, \quad (18)$$

where ΔE is the energy of dissociation at constant

[5] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929), especially p. 2314.

[6] This definition of entropy (differing by the thermodynamic entropy by a constant amount, which does not affect entropy differences) and the notation used in this part of the paper follow Rice and Gershinowitz, J. Chem. Phys. **2**, 853 (1934). The general form of entropy expression (Eqs. (14), etc.) is that which was used by Rice and Gershinowitz and independently suggested and discussed by Halford, J. Chem. Phys. **2**, 694 (1934) and further discussed by Eidinoff and Aston, J. Chem. Phys. **3**, 379 (1935).

volume per mole of $(NO)_2$. If we assume that, with change of V, the liquid acts like a perfect gas, then $\Delta H=\Delta E+P\Delta V=\Delta E+RT$, the extra energy being taken up by the liquid forces (P is internal pressure). Since it is obvious that

$$\Delta_0 S=\Delta_H S-\Delta_v S \tag{19}$$

it may be verified that Eqs. (17) and (18) are together equivalent to Eq. (4). This verifies the fact that the assumptions made about the liquid are equivalent to assuming that NO and $(NO)_2$ form a perfect solution.

We may now use Eq. (17) together with Eqs. (14), (15) and (16) to obtain a theoretical estimate of $\Delta_0 S$ to compare with the "experimental" value given by Eq. (19). In order to use Eq. (17), however, we need to know the value of V. An estimate of this quantity (which may without appreciable error be set equal to $V_H/2$) may be obtained on the basis of the assumption that the quantity $\Delta_H S$ is simply the change of entropy due to the change of volume when evaporation occurs from the normal unassociated liquid, i.e.,

$$\Delta_H S=R\ln(V_v/V_H)=R\ln(V_v/2V), \tag{20}$$

where V_v is the molar volume of the vapor phase at atmospheric pressure. We may assume that wherever they occur in logarithms, $N_1=N_1+N_2=N/2$. We then get from Eq. (17)

$$\begin{aligned}\Delta_0 S=N_1\Delta S^0&-(N_1/N)R\ln(V_v/N)\\&-(N_2/N)R\ln 2+(N_1/N)(\Delta_H S-R)\\&-(N_2/N)R\ln(N_2/N).\end{aligned} \tag{21}$$

In order to evaluate ΔS^0 we have to consider the quantities involved in Eq. (14). The quantities pertaining to NO molecules are easily obtained. B_2 can be found immediately; to get C_2 we take[7] $I_2=1.64\times10^{-39}$; $D_2=2$, on account of λ-type doubling, since NO is in a Π state (it is actually slightly greater than this, because the lowest state of NO is a doublet, but the upper doublet level is not very important at the boiling point of nitric oxide);[8] E_2 we assume to be equal to 1, which is a reasonably good approximation at this temperature.

[7] Sponer, *Molekülspektren*, I (Springer, Berlin, 1935), p. 36.

[8] See Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).

In order to evaluate the quantities for $(NO)_2$ we need to make some approximations about its structure. The unpaired electron of the NO molecule is a promoted π electron.[9] The wave function presumably has two nodal planes, one containing the line of centers of the atoms, and one perpendicular to that line. The energy of dissociation of $(NO)_2$ is probably sufficiently small so that the wave functions are not greatly distorted when the double molecule is formed. The formation of the double molecule presumably takes place in such a way that there is maximum overlapping of the wave functions, giving either a straight line structure O−N−O−N or a square

$$\begin{matrix}O-N\\|\quad|\\N-O\end{matrix}\quad\text{or}\quad\begin{matrix}O-N\\|\quad|\\O-N\end{matrix}.$$

(The selection of O−N−O−N rather than N−O−O−N, or O−N−N−O, is indicated by the fact that the thermodynamic entropy of solid nitric oxide does not become zero at 0°K, but approaches a value of $k\ln 2$ per molecule of $(NO)_2$; from this it seems likely that $(NO)_2$ has two distinct possible orientations of practically equal energy in the solid state.) We shall try both assumptions.

Let us first assume the square molecule. The translational factor, B_1, is again easily obtained. To get C_1 we divide it into two parts, C_1' and C_1'', the first involving the rotation in the plane of the square, and the second involving the rotations about axes in that plane. We first note that if the structure is

$$\begin{matrix}O-N\\|\quad|\\N-O\end{matrix}\quad\sigma_1'=2,$$

but since the square is probably not actually a true square, but a rectangle, we take $\sigma_1''=1$. (If the other square structure is correct $\sigma_1'=1$ and $\sigma_1''=2$, which gives the same final result.) However, it should be sufficiently good to assume it to be a true square with the normal NO distance in order to make an estimate of the moments of inertia. We thus get $I_1'=4I_2$ and $I_1''=2I_2$. We assume $D_1=1$. E_1 involves six translational degrees of freedom. Two of these will be like those of NO, and hence will introduce factors of 1 in E_1. The other four frequencies are undoubtedly low, and we shall take $E_1=2^4$, which

[9] Mulliken, Rev. Mod. Phys. **4**, 1 (1932). The rest of this paragraph is based on suggestions of Professor Mulliken, to whom I am grateful for discussing this problem with me.

corresponds to frequencies of approximately 60 cm^{-1}.

However, a correction to the above procedure is to be noted. The calculation of C_1 involves implicitly the assumption that the molecule $(NO)_2$ can rotate freely in the liquid, which is probably not true. In order to correct for this we shall assume that the three degrees of freedom of rotation are restricted in the same way and to the same extent as the three translational degrees of freedom. In other words, in order to calculate C_1 we shall first multiply by the correction factor V/V_0, where V_0 is the actual physical volume of the liquid, to be obtained from the observed density of the liquid.[10] This gives $V/V_0 = V_H/2V_0 = 0.058$. Making this correction, then, we obtain

$$\Delta_0 S = -8.4. \tag{22a}$$

If the straight line model for the double molecule is correct there is one less rotational degree of freedom and one more vibration. We therefore take $E_1 = 2^5$, and we shall calculate C_1 on the basis of the rough estimate $I_1 = 15I_2$. It is perhaps a little doubtful whether with only two degrees of freedom of rotation we should still correct C_1 by the same factor $V/V_0 = 0.058$. However, we shall do this, thus obtaining

$$\Delta_0 S = -8.7 \tag{22b}$$

not very different from the value for the square model.

Considering the uncertainties necessarily involved, these values seem to be in reasonably good agreement with the "experimental" value, 10.8. The discrepancy indicates that the motion of the double molecules is relatively more restricted than we have assumed.

[10] It may possibly be that we are exaggerating this effect for the double molecule, square model, as compared with the single molecule, which is assumed to rotate freely in the liquid. For it is true that the extension in space of the square double molecule is not much greater in any direction than that of the single molecule, and so it may be that the double molecule should be assumed to rotate more freely than allowed by our assumptions. If this is the case the discrepancy between the theoretical and experimental values of $\Delta_0 S$ is increased. This may, perhaps, be an argument in favor of the straight line model. While, as noted, we may be guilty of exaggerating somewhat the effect of the neighbors on the rotation in that case also, the exaggeration cannot be very great, as considerable inhibition of rotation seems certain to occur. It should, perhaps, be remarked that this correction is completely consistent with our previous assumptions about the liquid only if it is independent of the amount of association in the liquid.

§3.

From the measurements of Johnston and Weimer[3] or Eucken and d'Or,[1] it seems reasonable to infer that at the boiling point and atmospheric pressure the gas is about 1 percent associated. Using this estimate, we can apply Eq. (18) to calculate ΔE or ΔH for the gas phase. We shall insert into Eq. (18) the value of ΔS^0 from Eq. (19),* corrected, however, for the fact that in the gas phase the rotation of the double molecule is not restricted by the proximity of other molecules. This gives $\Delta E = 2630$ calories per mole of $(NO)_2$ or $\Delta H = 2870$. This differs from the value obtained for the liquid by about 1000 calories. It is perhaps, of some interest to note that the values for liquid and gas agree very well if we do not correct ΔS^0 to allow for the free rotation in the gas. This suggests that possibly there is free rotation in the liquid, and that the restriction of the motion of the molecules is due to their structure and applies also to the gas phase. The theoretical calculations speak against this, however, and it seems probable that the difference between the liquid and gas phases is real, though there is still the possibility that it is brought in by some of the assumptions and approximations we have made. These all seem quite reasonable, however, and it seems to me rather unlikely that all of the difference can be ascribed to this cause. It is, perhaps, not particularly astonishing in any event that the liquid forces should make a difference of 1000 calories in the heat of dissociation.

It is a pleasure to acknowledge the benefit of discussions with Professor J. H. Hildebrand.

It may be well to add a few words regarding the connection of this article with another recently published.[11] It may now be considered fairly definitely settled that the energy of dissociation of $(NO)_2$ is sufficiently great so that it may well act as an intermediate in the trimolecular oxidation of nitric oxide. The opportunity is also taken to mention some earlier papers, which were overlooked in my work on the oxidation of nitric oxide. A number of years ago Baker[12] and Hasche[12] presented evidence that this reaction is more complicated than usually supposed. If this is true the discussion of the points brought out in my paper is somewhat less urgent, though the principles laid down are naturally unaffected. Bodenstein,[13] however,

* I.e., the value consistent with the "experimental" value, 10.8, of $\Delta_0 S$.

[11] Rice, J. Phys. Chem. **4**, 53 (1936).

[12] Baker, J. Chem. Soc. (London) **65**, 611 (1894). Hasche, J. Am. Chem. Soc. **48**, 2253 (1926).

[13] Bodenstein, Zeits. f. physik. Chemie **B20**, 458 (1933).

believes, on the basis of his own experiments and those of his co-workers, that the reaction is simple—at least, he seems to feel that complications of the type envisaged by Baker and Hasche do not occur. More recently Bodenstein[14] has stated his belief that $(NO)_2$ is an intermediate and has cited the work of Eucken and d'Or[1] and Johnston and Weimer[3] as indicating its existence. He has also mentioned experiments which indicate that the change of temperature coefficient at low temperatures found by Briner, Pfeiffer and Malet[15] and discussed in my article does not actually exist.

It should, perhaps, be remarked that this correction is completely consistent with our previous assumptions about the liquid only if it is independent of the amount of association in the liquid.

[14] Bodenstein, Helv. Chim. Acta **18**, 745 (1935).

[15] Briner, Pfeiffer and Malet, J. Chim. Phys. **21**, 25 (1924).

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The Dipole Moments of the Alkali Halides

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THE dielectric constants of highly polar substances may not be determined in solution because of the polarity of the solvent necessary, nor in the vapor state at high temperatures because of the conductivity of the vapors, especially when in contact with metal surfaces. The only method available is the molecular ray method, and this method has been applied by Stern[1] and his collaborators to a number of substances under conditions which were not favorable to precise determinations of the moment. Because of the complicated situation produced by the superposition of the translational and rotational distributions on the space quantization of rotating dipoles in an electrostatic field, a very exact quantitative measurement of beam intensity is required for a calculation of the moment. Some years ago, one of the authors[2] found that the Taylor[3] hot filament detector worked as well for alkali halides as for alkali metals, and it was at once apparent that it would be possible to determine the moments of the alkali halides by the beam method. This research has been continued in various forms of apparatus for several years. The moments obtained were always of the same order of magnitude, but there were so many sources of uncertainty that publication has been delayed until these were eliminated so far as possible. A preliminary report of this work was given at the Oxford meeting of the Faraday Society in 1934. Since then, Scheffers[4] has published results for three salts obtained by using a method similar to ours. Our results are not in agreement with those of Scheffers. Possible reasons for the discrepancy will be discussed later in this article.

THE POLAR CHARACTER OF SALT MOLECULES

It may be predicted from general considerations of a chemical character and perhaps more definitely from wave mechanics considerations that the alkali halides should have a higher dipole moment than is ordinarily observed in diatomic molecules. If one assumes, as has usually been done, that this moment is of the order of magnitude of 10 Debye units, then a very simple consideration shows that a considerable tendency to association should exist. The situation in the saturated salt vapor at temperatures below the melting point of the salt is analogous to the situation in dilute solutions in a solvent of low dielectric constant, where Kraus[5] has found evidence of association. From familiar analogies one would expect this association to be limited to double molecules which would have zero moment, and one is thus led to the paradox that a high dipole moment should not be observed at all. This conclusion is evidently contrary to fact, and it is not possible to make any predictions as to association or how it should vary with the temperature of the

[1] I. Estermann and R. G. J. Fraser, J. Chem. Phys. **1**, 391 (1933).

[2] W. H. Rodebush and W. F. Henry, Phys. Rev. **39**, 386 (1932).

[3] J. B. Taylor, Zeits. f. physik. Chemie **57**, 242 (1929).

[4] H. Scheffers, Physik. Zeits. **35**, 425 (1934).

[5] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **57**, 1 (1935).

saturated vapor. It is possible that the associated molecules may have a greater moment than the single molecules. The moments reported here are the apparent moments as measured, and the question of association will be discussed elsewhere.

Method and Apparatus

The experiment consists in passing a beam of salt vapor through a Rabi type of electrostatic field and mapping the beam, with the field on and off by means of the positive ionization detector. An elaborate description of the apparatus is not necessary, since the various constituent parts of the apparatus have been described elsewhere.[6] A schematic drawing of the furnace slit system field plates and detector is shown in Fig. 1. In order to simplify the problem of alignment, the furnace, slit system, and field plates were mounted upon a metal base which was removable as a unit from the vacuum chamber. The vacuum chamber consisted of a brass tube of $4\frac{3}{4}$ in. internal diameter and 30 in. length. The ends of this tube were closed by glass plates which were ground to give a vacuum-tight joint when lubricated with a suitable stopcock grease. The vacuum was produced by glass pumps, using dibutyl phthalate as a vapor. These pumps were provided with the high speed turbine type of nozzles designed by Drs. Copley and Phipps[7] in this laboratory. With these pumps it was possible to maintain at all times a pressure of about 10^{-6} mm of mercury.

The furnace of tungsten steel was similar to the one designed by Lewis.[8] Tungsten coils were suspended in holes drilled in the walls of the furnace, the heat from the coils being transmitted by radiation. Some difficulty was experienced in early work with electrolysis of the salt. In order to avoid this, a special removable crucible was placed inside the furnace. This crucible was in contact with the furnace only at its base. The temperature of the furnace was controlled by a thermocouple, photoelectric cell, thyratron tube, set-up which proved to be highly satisfactory. In measuring intensities with the field, off and on, it is of the utmost importance to avoid temperature fluctuations. The temperature variations were ordinarily less than 0.2 degree. The accuracy with which the absolute temperature is known is of less importance for the measurement of the moments.

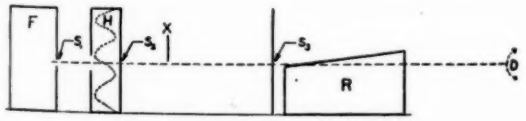

Fig. 1.

The plates for the Rabi type field were mounted 1.65 mm apart on quartz rods of sufficient rigidity to maintain the separation against the mechanical forces due to the electrostatic field. The electrostatic field was produced by the customary arrangement of transformer, kenotron and condenser. Elaborate tests were made to demonstrate the constancy of the field.

The detector consisted of a tungsten filament, cylindrical plate, and high sensitivity galvanometer. The detector filament was mounted eccentrically on a ground-glass joint, and the position of the filament was indicated by a protractor arm of $8\frac{1}{2}$ in. length. The filament was 0.05 mm in diameter. So far as the conditions of this experiment are concerned, two slits are sufficient to define the beam, but it was found simpler to use three slits in actual practice. In the simple design of furnace used, the outside of the slit was somewhat cooler than the inside, so that difficulty was experienced in keeping the slit free from deposited salt when the slit was small enough to define the beam. Accordingly, an intermediate slit, designated as a "heated slit," was introduced. This slit was cut in a nickel cylinder on the inside of which a tungsten filament was suspended so that the slit could be heated at frequent intervals to drive off salt deposits. It proved very satisfactory in operation.

The distance between the second and third slit was 5.7 cm. The distance from the third slit to the point of incidence of the field was 1.5 cm and the distance from the point of incidence to the detector filament was 7.6 cm. A magnetically controlled shutter was provided, so that the beam could be turned off and on at will.

[6] R. G. J. Fraser, *Molecular Rays* (Cambridge University Press, 1931).
[7] M. J. Copley and T. E. Phipps, Rev. Sci. Inst. **6**, 265 (1935).
[8] L. C. Lewis, Zeits. f. physik. Chemie **69**, 786 (1931).

The detection of beam intensity by the positive ion current is enormously complicated by the presence in the apparatus of a somewhat unsteady high potential on the field plates, which inevitably must affect the sensitive galvanometer required for detection. This difficulty was avoided by using the method introduced by Rabi[9] in which the salt molecules are deposited on a cold filament for a measured period of time. At the end of this period, the shutter is closed, the field on the plate switched off, and the filament is flashed, the resulting positive ion current being then measured by the ballistic throw of the galvanometer. Experiment shows that, when more than about five percent of the filament surface is covered, not all the alkali atoms come off as ions, so that the deflection is no longer proportional to the time of exposure. The limiting time of exposure, for which the deflections were proportional to the time, varied, as might be expected, with the size of the salt molecule for a given beam intensity. Most of the readings were made with an exposure period of three minutes. The galvanometer had a ballistic sensitivity of 4×10^{-11}.

Theoretical Considerations

The theory of the deflection of diatomic molecules in an inhomogeneous electrostatic field has been discussed by Fraser[6] and by Fraser and Estermann.[10] One is dealing here with a superposition of three distributions of the molecules in the field. These distributions are with respect to linear velocity, rotation and space quantization in the field. The moment that is effective in the deflection is the moment averaged over a complete rotation. Feierabend has made the very laborious calculation of the form of the distribution curve for a beam of zero width. In the actual experiment, however, we find that there are two further complications; the finite slit width and the finite width of the detector filament.

The latter quantity has an important bearing upon the design of the slit system, and will be considered first. When the beam is defined by two slits identical in size and shape, the intensity

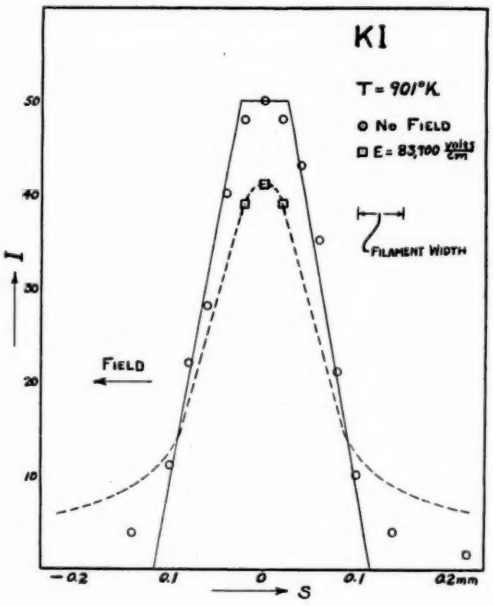

Fig. 2.

in the beam plotted against a space coordinate taken perpendicularly to both beam and slits forms a trapezoid (Fig. 2). The flat part of the trapezoid corresponds to the umbra, and the sides to the penumbra. This is for the undeflected beam. With the field on, the intensity curve is altered in a way that may be approximately described as a trapezoid of lower altitude and broader base. It turns out that the most important measurements are the altitudes of the trapezoids in the two cases. In order that the altitude be measured with certainty, the flat part of the beam should be at least as wide as the detector filament. In order to obtain the maximum sensitivity, which means the maximum decrease in the altitude of the trapezoid when the field is on, the beam should not be wider than this. The best conditions, therefore, appear to be obtained when slits and detector filament are of the same width. In our experiments the slits were approximately 0.05×0.5–0.8 mm.

As the detector filament is moved through the beam, the "corners" of the trapezoid are rounded off and "tails" are produced by the overlapping, so that the actual curve of galvanometer deflections obtained is that corresponding to the circles (Fig. 2). If the geometry of the slit system is known with sufficient exactness, the trape-

[9] I. I. Rabi and V. W. Cohen, Phys. Rev. **46**, 707 (1934).
[10] I. Estermann and R. G. J. Fraser, J. Chem. Phys. **1**, 390 (1933).

zoidal curve may be inferred from the actual curve obtained, but the only points on the two curves that correspond are the maximum and the mid-portions of the sides. If a sufficient number of readings are taken, a satisfactory correspondence may be established between the curve of galvanometer deflections and the true trapezoidal intensity curve, but experience has shown that the true intensity curve may be calculated from the geometry of the slits, provided they are carefully constructed, with an accuracy quite equal to that obtained by careful mapping of the actual beam by galvanometer deflections. The measurement on the undeflected beam is, therefore, in practice limited to the measurement of the maximum intensity.

Similarly, for the deflected beam, it turns out that the only measurement of significance is the maximum intensity. Since, in deflection experiments of this character, the two maxima apparently coincide in space, when once the position of the maximum has been located a series of readings may be taken with the field alternately on and off without moving the filament.

The intensity curve of the deflected beam may be considered as a distorted trapezoid lowered and broadened with sides which are no longer straight lines.

The upper corners of the trapezoid will also be rounded off so that the top of the trapezoid is no longer flat, and the maximum reading obtained with the detector filament is not the actual maximum intensity of the beam, but something less. It is not possible to reconstruct the intensity curve, therefore, from galvanometer deflections with any certainty, except in the edges of the beam where the intensity is too low to permit accurate determinations. It is possible, however, to assume an approximate value of the moment and calculate the exact shape of the curve in the neighborhood of maximum intensity from theoretical considerations. The exact shape of the curve being known, it is, therefore, possible to calculate the exact maximum intensity from the galvanometer reading, and hence the true value of the moment as a second approximation. In our experiments, the actual galvanometer readings of maximum intensity were shown to be about one percent too low.

The general shape of the intensity curve with the field on is given by the dotted line in Fig. 2. This shows the general characteristics of similar curves obtained in beam experiments in that the upper part of the curve does not appear changed in shape, but only decreased in height.

The dipole moment is, therefore, calculated from the percentage decrease in maximum intensity of the beam when the field is applied and the accuracy depends upon the accuracy with which this percentage decrease is measured. The percentage decrease may be made greater in magnitude by decreasing slit width and increasing the distance between the field and detector filament, but this change is accompanied by a decrease in the magnitude of the deflection so that there is no advantage in changing dimensions of the apparatus beyond a certain point. Similarly, increasing the sensitivity of the galvanometer does not increase the reliability of the measurements. A possible way of increasing the precision of the measurements would be to increase the strength of the field on the Rabi plates, but there are practical limitations here too.

We have finally to consider the effect of finite slit width on the calculation of the moment. The curve calculated by Feierabend, previously referred to, gives the distribution of the intensity in a beam from slits of infinitesimal width. We may represent the Feierabend curve as a function of the deflection in mm $P_{(s)}$. The intensity curve of the undeflected beam may be represented in a similar way as $f_{(s)}$, where s is now the displacement of the detector filament in mm. It has been shown by Estermann[10] that the intensity at the maximum of the deflected beam is given by the integral

$$I=\int_{-\infty}^{+\infty} f_{(s)}P_{(s)}ds.$$

The integral must be obtained by quadrature, since the function $P_{(s)}$ is not known. The values for $P_{(s)}$, as given by Feierabend, are not given for actual deflection, but for an argument,

$$\sigma=s/s_0,$$

where s is the actual deflection, and s_0 is the deflection that a molecule would experience when in certain quantum states that are taken as an

TABLE I.

DATA FOR SAMPLE RUN KI

Temperature	.901°K
Field intensity	83,700 volts/cm
Average maximum intensity undeflected beam	64.8
Average maximum intensity deflected beam	55.3
Distance field plates to detector	76 mm
θ	7° 48′
s_0	0.00263 mm
μ	11.1×10^{-18} l.s.

TABLE OF RESULTS

SALT	TEMPERATURE	$\mu\times10^{18}$	RESULTS OF SCHEFFERS
KCl	949°K	9.74	6.3 (1023°K)
	"	9.74	
	"	9.25	
	"	9.40	
	"	9.54	
KBr	916	10.8	
	925	10.9	
KI	894	11.0	6.8 (950°K)
	901	11.1	
CsI	873	12.1	

average or standard state. s_0 is actually given by the equation

$$s_0=\mu^2E^2l/8(kT)^2\tan\theta,$$

where kT is the Boltzmann factor, E the field intensity, l the distance from the point of incidence to the detector filament and θ is the angle between the incident beam and the field plates.

μ is, of course, the dipole moment, and the calculation of the maximum intensity of the deflected beam is made by assuming different values of μ until one is obtained which gives a value in agreement with the experimental results.

By reference to Table I, it is seen that the values as calculated from our experiments are much greater than those obtained by Scheffers. The order of arrangement of the salts according to moment appears to be the same in the two experiments. A rough prediction of this order could be made from a consideration of the ionic radii.

Scheffers' results are at higher temperatures and pressures than ours. The discrepancy between the two sets of experiments could be accounted for by association. Until the question of association is settled, one may not draw conclusions as to the actual moment of the molecules.

Scheffers used an inhomogeneous electrostatic field produced by a wire and concentric cylinder. This type field gives a greater deflection, but it is necessary to locate the beam with exactness with respect to the wire. The Rabi type of field does not introduce any serious uncertainty so long as the angle of incidence is not made too small, but it does not give as large a deflection. We have tested the Rabi field for "end effects" by changing the point of incidence of the beam. No change in the apparent moment was observed. We have not checked the calculation of Fraser that the effective square of the electric moment is 0.6 times the field between the plates. If this conclusion is in error, then our results would be in error by a corresponding amount.

It is difficult to estimate errors in a measurement which involves so many variables in such a complicated way, but with a great many measurements made under different conditions we have never obtained more than a ten percent variation in the effective moment.

In every case we tested the beams for ions by applying a low field to the Rabi plates, but only in the case of cesium fluoride did we observe an appreciable diminution of intensity.

The purity of the salts used was tested. They were shown to be free from appreciable amounts of impurities.

The fact the dipole moments obtained are of the order of magnitude expected and increase with the ionic radii may be considered as evidence favoring the conclusion that the salt vapors contain single molecules only. The density of salt vapors has been investigated at some length in this laboratory by Dr. V. Deitz, and the results of his investigations will be published elsewhere.

The dipole moment obtained indicates that a mixture of the ionic and homopolar types of bonding prevails in salt molecules. If the bonding were purely ionic in character, a still larger dipole moment would be anticipated than has been observed.

The authors wish to acknowledge their indebtedness to Drs. M. J. Copley and T. E. Phipps of this laboratory for many helpful suggestions.

Determination of Molecular Structure by Electron Diffraction

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(Received February 21, 1936)

(1) An apparatus has been designed and built for the purpose of determining molecular structure by electron diffraction using 6400 volt electrons. (2) The apparatus was checked with carbon tetrachloride whose structure is accurately known, and the interatomic distances in, and configurations of, a number of compounds determined. (3) Ethylene oxide was found to be a three membered ring with a carbon-carbon distance of 1.56±0.05A, a carbon-oxygen distance of 1.45±0.05A and a carbon-hydrogen distance of 1.05±0.07A. (4) Sulfur monochloride was found to have the two chlorine atoms attached to different sulfur atoms, the sulfur-sulfur distance was found to be 2.04±0.05A, the sulfur-chlorine distance of 1.98±0.05A and an angle of 105±5° between bonds. (5) In acetaldehyde the carbon-oxygen distance was found to be 1.20±0.05A, the carbon-carbon distance 1.51±0.05A and the bond angle 122±5°. (6) Paraldehyde was found to have a puckered ring structure with a carbon-oxygen distance of 1.41±0.05A, a carbon-carbon distance of 1.52±0.05A and the tetrahedral angle of 109° between bonds.

SINCE the original work of Mark and Wierl,[1] the results of many investigators[2] have shown that electron diffraction methods provide a very useful tool for determining molecular structure. The object of the experiments reported here was to extend this work and to determine if much lower voltages (6500 volts instead of 20 to 50 kilovolts) might not be used in electron diffraction apparatus for determining molecular structure.

In the interpretation of the experimental results the complete formula for the coherent scattered intensity, given below, was not used. In this formula

$$I \propto \sum_{i,\,j}^{n} \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}}, \qquad (1)$$

where $\psi_i = (Z_i - F_i)/\mu^2$

and $x_{ij} = (4\pi \sin \tfrac{1}{2}\theta/\lambda) l_{ij} = \mu l_{ij}$

Z and F being the atomic number and form factor for the ith atom, l_{ij} the distance between the ith and jth atoms, the summation being taken over all the atoms of the molecule. As Pauling and Brockway[3] have pointed out, when the maxima and minima of intensity are measured by visual means, as was done here, the simpler formula, given below, usually suffices.

$$I' \propto \sum_{i,\,j=1}^{n} Z_i Z_j \frac{\sin x_{ij}}{x_{ij}} \qquad (2)$$

where $I' = I \cdot f(\theta)$ and $f(\theta)$ is a monotonic function of the angle, θ. The difference between the two formulae is greatest at small angles, and preliminary calculations with a model of ethylene oxide similar to that finally used gave for the positions of the first maximum by the two formulae of 4.17 and 4.21×10^{-8}, the difference being less than the experimental error. From the experimental curves given by Mott and Massey[4] we may conclude that the scattering by single atoms is still proportional to $((Z_i - F_i)/\mu^2)^2$ for voltages as low as 2000 volts except for very heavy atoms or very large angles of scattering. Hence we may feel sure that our formula (1) and consequently (2) will be valid for the 6400 volts used.

DESCRIPTION OF APPARATUS AND METHOD

The general design of the apparatus follows that of Hendricks,[5] except that a filament was used as a source of electrons rather than a discharge tube. The filament was a flat spiral of platinum wire coated with barium oxide, and

* Adapted from a thesis submitted to The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Mark and Wierl, Physik. Zeits. **31**, 366, 1028 (1930).

[2] Especially Pauling and his co-workers: Pauling and Brockway, Proc. Nat. Acad. Sci. **19**, 860 (1934); Brockway and Wall, J. Am. Chem. Soc. **56**, 2373 (1934); Sutton and Brockway, J. Am. Chem. Soc. **57**, 473 (1935); and also Dornte, J. Chem. Phys. **1**, 566, 602 (1933) and de Laszlo, Proc. Roy. Soc. **A146**, 672 (1934).

[3] Pauling and Brockway, J. Chem. Phys. **2**, 867 (1934).

[4] Mott and Massey, *The Theory of Atomic Collisions* (Oxford University Press, 1933), p. 122.

[5] Hendricks, Maxwell, Moseley and Jefferson, J. Chem. Phys. **1**, 549 (1933).

was so mounted that it could be moved from outside the apparatus to give the best electron beam intensity. Eastman process plates were used to record the scattered electrons, but because of the slight effect of the low voltage electrons on the plates it was found advisable to oil them. The distance from the jet through which the gas issues to the photographic plate was 7.45 cm. The whole apparatus was mounted so that the path of the electron beam made an angle of 45 degrees with the horizontal and was in the direction of the earth's magnetic field so as to reduce the effect of this field on the beam as far as possible.

The high potential was secured from a 110–7000 volt transformer using two General Electric PJ-24 tubes for full wave rectification. The pulsations were smoothed out by means of a 0.5 microfarad condenser and a choke coil. The filament was heated by the current from another transformer and the filament temperature controlled by a variable resistance in the primary circuit of this transformer. The voltage applied across the apparatus was determined by measuring the current through a calibrated high resistance of eight megohms.

Experimental Results

As a check on the apparatus and in order to become familiar with the interpretation of the actual photographs, it was decided to first study a compound whose structure was already known. Carbon tetrachloride was chosen for this because of the accurate data which are available for this compound. The C. P. material was distilled under a vacuum into the bulb from which it was to be vaporized and there several times alternately frozen and melted while under a vacuum to eliminate as much as possible of the dissolved air. During the run the material was kept at 0°C by means of an ice bath, and exposures of from 4 to 32 seconds were taken. The results are tabulated in Table I below. The experimental figures represent the average of measurements on twelve plates, the deviation of any measurement from the average being not more than two percent. The accelerating voltage was 6400 volts which corresponds to a wave-length of 0.1531A. The calculated values are based on a chlorine-carbon distance of 1.77A which compares very favorably with the value of 1.76A found by Brockway and Wall[2] and by de Laszlo and Cosslet[6] and the value of 1.78A found by Braune and Knoke.[7]

Table I. *Carbon tetrachloride.*

	Values of $\mu \times 10^8$	
	Observed	Calculated
Maximum	2.71	2.69
Minimum	3.76	3.74
Maximum	4.80	4.79
Minimum	5.97	5.96
Maximum	7.16	7.16

Pauling and Brockway[3] have indicated that the interatomic distances measured by electron diffraction can be used to calculate a series of covalent radii for the various atoms. Because of the fact that the structural formula for ethylene oxide is usually written as a three membered ring, it was thought that in this compound the carbon-oxygen distance might be slightly different from that in acyclic compounds. The ethylene oxide, taken from a commercial tank, was carefully distilled, the fraction taken for use having a boiling point range of less than one degree. The compound was kept at −40°C during the run, this temperature being found to give the optimum vapor pressure. Because of the small scattering power of ethylene oxide, exposures up to 300 seconds were necessary. The experimental values of μ are given in Table II and are the average of measurements on nine plates. The calculated values are based on a carbon-oxygen distance of 1.45A and a carbon-carbon distance of 1.56. In compounds of low scattering power it may be necessary to take the scattering by the hydrogen atoms into account; this was done here using a carbon-hydrogen distance of 1.05A and although the calculated values were not very sensitive to small changes in this distance, including these terms does have an appreciable

Table II. *Ethylene oxide.*

	Values of $\mu \times 10^8$	
	Observed	Calculated
Maximum	5.34	5.37
Minimum	7.46	7.48
Maximum	9.58	9.55

[6] de Laszlo and Cosslet, Nature **134**, 63 (1934).
[7] Braune and Knoke, Zeits. f. physik. Chemie **B21**, 297 (1933).

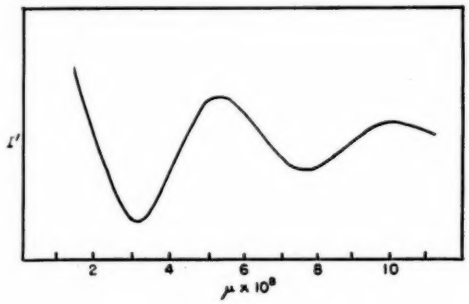
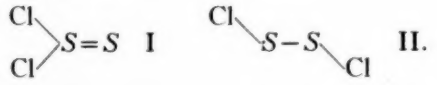


FIG. 1. Theoretical intensity curve for ethylene oxide.

effect. The theoretical intensity curve is given in Fig. 1. The carbon-carbon distance found above is in good agreement with the distance of 1.54A found by Dornte.[2] The carbon-oxygen distance compares quite favorably with the distance of 1.44A found by Sutton and Brockway[2] in dimethyl ether. These results, together with the fact that no alternative structure could be found which would give any agreement with the experimental points, indicates that ethylene oxide is a three-membered ring in which the interatomic distances are nearly the same as in acyclic compounds. Alternate structures in which the oxygen atom was at a greater distance from one carbon atom than from the other gave no agreement with experiment.

The structure of the compound, sulfur monochloride, is not definitely established. The available chemical evidence does not seem to be sufficient to distinguish between the two alternative structural formulae given below, though it does seem to favor formula II.



For this reason it was decided to study this compound by electron diffraction to see if more light could be thrown on the subject. Merck's sulfur monochloride was carefully distilled in a vacuum from a receiver containing a quantity of free sulfur and activated bone charcoal to remove impurities. The material was kept at 30°C during the runs and exposures of from 10 to 200 seconds were taken. The results, given below, are the average of measurements on eleven plates. The calculated values were obtained by using formula II, a chlorine-sulfur distance of 1.98A, a sulfur-sulfur distance of 2.04A and an angle of 105° between bonds. In the structure II for sulfur monochloride it is probable that there would be some free rotation about the sulfur-sulfur bond. Accordingly with the use of the above structure, distances, and angles, the theoretical curve was calculated for three different positions of the two chlorine atoms. In Table III,

TABLE III. *Sulfur monochloride.*

	Observed	Values of $\mu \times 10^8$ Calculated		
		A	*B*	*C*
Maximum	4.12	4.20	4.13	4.17
Minimum	5.55	5.44	5.50	5.44
Maximum	6.68	6.64	6.70	6.63
Maximum	7.83	8.10	7.86	7.60
Minimum	8.90	9.04	8.93	9.07
Maximum	10.21	10.27	10.16	10.32

A gives the values of μ when the shortest possible chlorine-chlorine distance consistent with the above structure was used, *B* the results when an average distance based on free rotation was used, and *C* the results when the longest possible distance was used. It will be noted that *B* agrees best with the experimental results. When similar calculations are carried out using different values for the sulfur-sulfur and sulfur-chlorine distances, the results obtained do not agree at all with experiment for any relative positions of the atoms. The theoretical intensity curve for this structure is given in Fig. 2.

While these results are not in such good agreement with the values of 2.05 and 2.10A, respectively for the two distances which one would obtain by the use of Pauling and Huggins[8] table of covalent radii, they are in favor of the second of the two formulae given for sulfur monochloride.

Acetaldehyde and its polymer, paraldehyde, were also studied. The acetaldehyde was prepared by distilling it from C. P. paraldehyde to

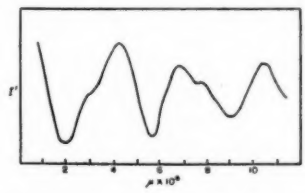


FIG. 2. Theoretical intensity curve for sulfur monochloride.

[8] Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).

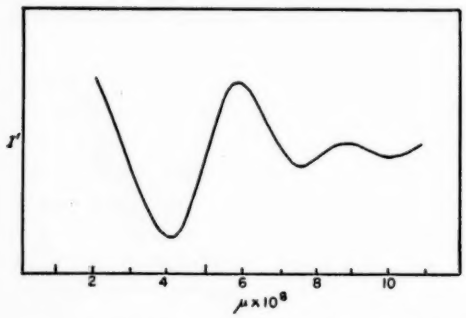


FIG. 3. Theoretical intensity curve for acetaldehyde.

which a few drops of sulfuric acid had been added. The runs were made in the usual manner. The material was kept at −35°C in the bulb and exposures up to 300 seconds were taken. The results, Table IV, are the averages of measurements on ten plates. The theoretical intensity curve is given in Fig. 3. The calculated values were obtained by using a carbon-carbon distance of 1.51A, and oxygen-carbon distance of 1.20A and an angle of 122° between the two bonds. Due to the fact that only two maximum could be measured, the structure could not be determined uniquely, but that given does show good agreement with the experimental measurements and with other measurements of these distances.

For paraldehyde the runs were made in the usual manner, the material being kept at 30°C during the runs and exposures up to 200 seconds were taken. The results, Table V, are the averages of measurements on eleven plates.

For the calculation of the values of μ tabulated in Table V and the theoretical curve given in Fig. 4, a structural formula must be assumed for

TABLE IV. *Acetaldehyde.*

	Values of $\mu\times10^8$	
	Observed	Calculated
Maximum	5.92	5.91
Minimum	7.60	7.61
Maximum	8.74	8.72

TABLE V. *Paraldehyde.*

	Values of $\mu\times10^8$		
	Observed	Calculated	
		A	*B*
Maximum	3.40	3.43	3.44
Minimum	4.41	4.45	4.20
Maximum	5.69	5.67	5.79
Minimum	7.47	7.46	7.47
Maximum	9.24	9.22	9.16

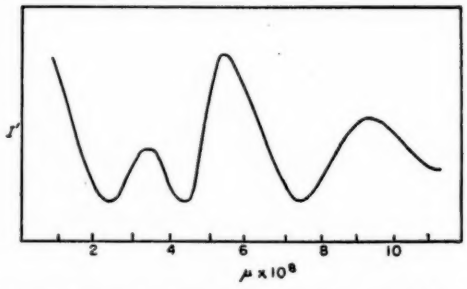
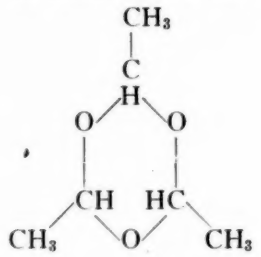


FIG. 4. Theoretical intensity curve for paraldehyde.

the molecule. The one used is the usual ring formula for paraldehyde with a puckered ring, i.e., the carbon and oxygen atoms are not all in the same plane. The carbon-oxygen distance was taken to be 1.41A, the carbon-carbon distance as 1.52A with the angle between the bonds the tetrahedral angle of 109° 28′ 16″. The relative positions of all the carbon and oxygen atoms is given by the statement that if the plane formula



be taken as the projection of the molecule on the plane of the paper, the projected ring would form a regular hexagon, and that if the ring carbon atoms were in the plane of the paper, the oxygen atoms would be a distance of $1.41\times\sin 19°\,28'\,16''=0.47$A above this plane and the three methyl carbon atoms a distance of $1.52\times\sin 19°\,28'\,16''=0.51$A above this plane. The formula used to calculate the intensity then becomes

$$I\sim 576\left[\frac{\sin 1.41\mu}{1.41\mu}+\frac{\sin 2.3932\mu}{2.3932\mu}\right]+600\frac{\sin 2.3025\mu}{2.3025\mu}$$
$$+432\frac{\sin 3.6506\mu}{3.6506\mu}+288\left[\frac{\sin 2.7186\mu}{2.7186\mu}+\frac{\sin 4.0919\mu}{4.0919\mu}\right]$$
$$+216\left[\frac{\sin 1.52\mu}{1.52\mu}+\frac{\sin 4.7847\mu}{4.7847\mu}\right].$$

This structure gives the values of μ for the maxima and minima marked *A* in the table. If we use the similar structure in which the

methyl carbon atoms are directly below the other carbon atoms a distance of 1.52A, we get the values of μ marked B in the table. The difference is not very marked but it is sufficient to make it probable that the methyl carbon atoms are, as we have sketched them, above the plane of the oxygen atoms.

Discussion of Results

While an apparatus has been developed by which one may make measurements of interatomic distances by means of the diffraction of electrons of only 6400 volts energy, the accuracy of the results is not as great as that of other workers using higher voltages. In the experiments reported here, the accelerating voltage was known with an accuracy of one percent. The ammeter and resistance used were thus accurate, the choke coil and condenser were sufficient to smooth out the pulsations of the rectified 60-cycle alternating current to this degree of accuracy, and the actual measurements showed that the variations in the input alternating current were no greater than this.

The distance from the jet to the photographic plates could be measured quite accurately, the error here being certainly less than one percent. The greater error is in the actual measurement of the positions of the maxima on the plates. This is especially true since the maxima are not sharp lines but are rather broad. The fact that the measurements from the individual plates do not differ from the average by more than 3 percent indicates that the maxima can be determined fairly accurately. The final values of μ are probably accurate to within two percent. The relation between the positions of the maxima and the values of the interatomic distances is, in general, quite complicated, so that for a given error in the former it is difficult to estimate the error in the latter.

A real source of error in these experiments comes from the fact that only a few maxima and minima could be measured due to the limitations of the apparatus. When this is true, the fact that the observed and calculated values of μ agree very well is not a guarantee of like accuracy in the values of the interatomic distances. For small variations in the structure are best detected in the positions of the outer maxima, those beyond the third. It is difficult to say just how much effect this would have on the compounds studied here, but it is probable that the measurements recorded are accurate to ± 0.05A.

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The Application of the Three-Dimensional Patterson Method and the Crystal Structures of Proustite, Ag_3AsS_3, and Pyrargyrite, Ag_3SbS_3*

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It is shown that the three-dimensional Patterson method can be so simplified by the use of the symmetry properties of the crystal under consideration that its use in determining the positions of atoms in crystals is practicable. This method is then used to determine the positions of the heavy atoms in proustite, Ag_3AsS_3. The positions of the sulfur atoms are found by the use of the covalent atomic radii and assumptions concerning bond directions. The structure so derived is found to be compatible with the observed data. Proustite is found to contain pyramidal AsS_3''' groups and silver atoms forming two bonds to sulfur in almost opposed directions. Pyrargyrite, Ag_3SbS_3, is found to have almost the same structure as proustite. The analytical statement of the structures is as follows:— The space group, C_{3v}^6-R3c, is common to both proustite and pyrargyrite. The special positions of C_{3v}^6 are (in hexagonal axes)

(2a) $0, 0, Z$; $0, 0, \frac{1}{2}+Z$;

(6b) X, Y, Z; $\bar{Y}, X-Y, Z$; $Y-X, \bar{X}, Z$;
$\bar{Y}, \bar{X}, \frac{1}{2}+Z$; $X, X-Y, \frac{1}{2}+Z$; $Y-X, Y, \frac{1}{2}+Z$;

and positions derived from these by the operations of the rhombohedral lattice. The parameter values are:

Proustite		Pyrargyrite	
$a_0=10.74$A,	$c_0=8.64$A	$a_0=11.04$A,	$c_0=8.71$A
2As in 2a,	$Z_{As}=0.000$	2Sb in 2a,	$Z_{Sb}=0.000$
6Ag in 6b,	$X_{Ag}=0.246$	6Ag in 6b,	$X_{Ag}=0.250$
	$Y_{Ag}=0.298$		$Y_{Ag}=0.305$
	$Z_{Ag}=0.235$		$Z_{Ag}=0.210$
6S in 6b,	$X_S=0.220$	6S in 6b,	$X_S=0.220$
	$Y_S=0.095$		$Y_S=0.105$
	$Z_S=0.385$		$Z_S=0.355$

Introduction

THE determination of the inner structure of a crystal by means of x-rays has been, in most cases, a process of trial and error. Once the space group of the crystal is known, the direct use of the x-ray data is abandoned. A structure which satisfies the symmetry requirements of the space group is then assumed and the intensities of the diffracted x-ray beams are calculated on this basis. If these do not agree with the experimentally determined intensities, another structure is assumed and the process is repeated. Systematic methods of carrying out this process have been devised which are remarkable for the rapidity and accuracy with which, in some cases, they lead to the elimination of every structure but the true one. In other cases, however, the systematic trial and error method breaks down and either fails completely or leads to the loss of much time.

If a convenient direct method for calculating the structure of a crystal from the experimental data were available, these inefficiencies and failures would, of course, be eliminated. Such a method has not as yet appeared. However, a very close approximation to such a treatment is provided by the Patterson method when used as described in the next section.

The determination of the structure of proustite by means of this method is described later in this paper and illustrates the advantages and limitations of the treatment.

Use of the Three-Dimensional Patterson Method

Patterson[1] has shown that the three-dimensional Fourier series

$$P(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \cos 2\pi(hx+ky+lz)$$

—where x, y and z are the coordinates of points in the crystal lattice measured in units of the primitive translations and $F_{(hkl)}$ is the amplitude of the diffracted beam "reflected" from the crystal plane with indices (hkl)—represents a function having maxima at vector distances from the origin equal to vector distances between pairs of maxima in the electron density in the crystal. Since there is a maximum in the electron density at the center of each atom, the coordinates of the maxima in $P(x, y, z)$ can be interpreted as the components of interatomic vectors. The evaluation of such a series at a sufficient number of points in the unit cell to show the true form of the function $P(x, y, z)$ has never been carried out, the calculation involving a prohibitive amount of labor. Instead, the projection of $P(x, y, z)$ on a plane perpendicular to one of the crystal axes has been used. If the projection is upon the plane perpendicular to the z axis, the projected function $p(x, y)$ is calculated thus

$$p(x, y) = \int_0^1 P(x, y, z)dz = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \int_0^1 \cos 2\pi(hx+ky+lz)dz$$

$$= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty}{}' |F_{(hk0)}|^2 \cos 2\pi(hx+ky).$$

$p(x, y)$, which is represented by a two-dimensional Fourier series, has been evaluated completely by several authors in the course of various crystal structure investigations. Its use has proved very fruitful, in some cases making possible the determination of structures which would have been impracticably difficult otherwise.

The use of $p(x, y)$ has, however, two disadvantages. In the first place, there is a large probability that a given maximum is composed of the superposition of two or more maxima of $P(x, y, z)$ which have projected onto nearly the same spot. Secondly, the resolution of maxima which are near together is not as good as can be obtained by the use of $P(x, y, z)$, since only a small fraction of the terms in $P(x, y, z)$ are used in $p(x, y)$. The function $P(x, y, z)$ would consequently be preferred if the labor involved in its calculation could be reduced.

The use of the symmetry of the crystal under consideration often leads to the desired simplification. For example, let the crystal have a

* Contribution No. 535 from Gates Chemical Laboratory, California Institute of Technology.

[1] A. L. Patterson, Zeits. f. Krist. **90**, 517 (1935).

twofold axis (which will be taken coincident with the b axis). Then, if there is an atom at the point (x, y, z), there will be another atom, crystallographically equivalent to the first, at $(\bar{x}, y, \bar{z})$. The vector between these atoms has the components $(2x, 0, 2z)$ and consequently there will be a maximum in $P(x, y, z)$ at the point $(2x, 0, 2z)$. This maximum lies in the plane $y=0$. There will be a maximum in this plane for each (crystallographically) different kind of atom in the crystal. The x and y coordinates of all the atoms in the crystal can consequently be found by evaluating $P(x, y, z)$ for $y=0$ only. In this case the expression for $P(x, y, z)$ can be simplified as follows:

$$P(x, 0, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \cos 2\pi(hx+lz)$$

$$= \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \cos 2\pi(hx+lz) \times \left\{ \sum_{k=-\infty}^{\infty} |F_{(hkl)}|^2 \right\}.$$

Now let $$\sum_{k=-\infty}^{\infty} |F_{(hkl)}|^2 = C_{hl}$$

and we have

$$P(x, 0, z) = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{hl} \cos 2\pi(hx+lz).$$

$P(x, 0, z)$ is a two-dimensional Fourier series of the same general type as $p(x, y)$ and consequently its calculation is practicable. The same information about the x and z coordinates of the atoms is contained in $P(x, 0, z)$ as in $p(x, z)$, but in much clearer form; for (a) the maxima in $P(x, 0, z)$ will be sharper, in general, since there are usually more terms in its Fourier series than in that of $p(x, z)$ and (b) all the maxima corresponding to interatomic vectors not parallel to the plane $y=0$ appear in $p(x, z)$, but are eliminated in $P(x, 0, z)$. $P(x, 0, z)$ can be used to determine the x and z coordinates of atoms in case the b axis is parallel to a two-, three-, four-, or sixfold symmetry axis of the crystal, for in all these cases the vectors between equivalent atoms are parallel to the plane $y=0$.

In case the b axis is a twofold screw axis the treatment of $P(x, y, z)$ is slightly changed. The coordinates of equivalent atoms are now (x, y, z) and $(\bar{x}, y+\frac{1}{2}, \bar{z})$ and the vectors between equivalent atoms have components $(2x, -\frac{1}{2}, 2z)$. In this case $P(x, y, z)$ must be evaluated for $y=-\frac{1}{2}$ or, since $P(x, y, z)$ has a center of symmetry, for $y=\frac{1}{2}$. The calculation simplifies as follows:

$$P(x, \tfrac{1}{2}, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \cos 2\pi(hx+k/2+lz)$$

$$= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} (-1)^k |F_{(hkl)}|^2 \times \cos 2\pi(hx+lz)$$

$$= \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{hl} \cos 2\pi(hx+lz),$$

where $$C_{hl} = \sum_{k=-\infty}^{\infty} (-1)^k |F_{(hkl)}|^2.$$

It is easily seen what changes in the calculation must be made for threefold, fourfold and sixfold screw axes.

If the crystal contains a plane of symmetry, the form to which $P(x, y, z)$ reduces is even simpler than in the case of an axis of symmetry. Suppose the plane is perpendicular to the b axis. Then there are equivalent atoms at (x, y, z) and $(x, \bar{y}, z)$. The vector between these atoms has components $(0, 2y, 0)$ and the corresponding maximum in $P(x, y, z)$ lies on the b axis. To find this maximum it is only necessary to evaluate $P(0, y, 0)$. The calculation is as follows:

$$P(0, y, 0) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \cos 2\pi ky$$

$$= \sum_{k=-\infty}^{\infty} B_k \cos 2\pi ky$$

with $$B_k = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2.$$

This is a one-dimensional Fourier series and can be completely evaluated in a few hours. In the case of a glide plane the calculation is equally simple. In this case there are equivalent atoms at (x, y, z) and $(x, \bar{y}, z+\frac{1}{2})$ (the glide is taken to be

along the c axis) and there will be a maximum in $P(x, y, z)$ at $(0, 2y, \frac{1}{2})$. The simplification of $P(x, y, z)$ takes place thus,

$$P(0, y, \tfrac{1}{2}) = \sum_{k=-\infty}^{\infty} B_k \cos 2\pi k y$$

with $$B_k = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} (-1)^l |F_{(hkl)}|^2.$$

In Table I is given a summary of the forms of $P(x, y, z)$ best suited to the various symmetry elements. It is to be noted that at least one of these forms is available for the study of any crystal that is not triclinic.

TABLE I. *Forms of $P(x, y, z)$ best suited to the determination of atomic coordinates in crystals having various symmetry elements.*

	Symmetry Element	Form of $P(x, y, z)$
(a)	Axes parallel to b-axis	
	(i) 2, $\bar{4}$, 4_2, $\bar{4}$, 6, 6_2* $\bar{3}$, $\bar{3}$, 6_3	$P(x, 0, z)$
	(ii) 2_1, 4_1, 4_3, 6_1, 6_5	$P(x, \frac{1}{2}, z)$
	(iii) 3_1, 6_2, 6_4	$P(x, \frac{1}{2}, z)$
(b)	Planes perpendicular to b-axis	
	(i) reflection planes	$P(0, y, 0)$
	(ii) glide plane, glide $=\frac{1}{2}a_0$	$P(\frac{1}{4}, y, 0)$
	(iii) " " " $=\frac{1}{2}c_0$	$P(0, y, \frac{1}{4})$
	(iv) " " " $=\frac{1}{2}(a_0+c_0)$	$P(\frac{1}{4}, y, \frac{1}{4})$
	(v) " " " $=\frac{1}{2}(a_0+c_0)$	$P(\frac{1}{4}, y, \frac{1}{4})$
	(vi) " " " $=\frac{1}{4}(3a_0+c_0)$	$P(\frac{1}{4}, y, \frac{1}{4})$

In cases (a) x and z are determined for each atom.
In cases (b) y is determined for each atom.
* The nomenclature of symmetry axes is taken from the "Internationale Tabellen zur Bestimmung von Kristallstrukturen."

There are other cases in which the values of some of the atomic coordinates in a crystal can be determined by the evaluation of $P(x, y, z)$ throughout a plane or along a line only. For instance, it might be known from symmetry considerations that the position (0, 0, 0) is occupied by an atom and that there are other atoms in the plane $y=\frac{1}{2}$ with coordinates (say) $(x_1, \frac{1}{2}, z_1)$, $(x_2, \frac{1}{2}, z_2)$, etc. Then there will be maxima in $P(x, y, z)$ at just these points, for vectors from the origin to these atoms are also interatomic vectors. The evaluation of $P(x, \frac{1}{2}, z)$ would determine the x and z coordinates of all these atoms. Or, for another example, suppose again that (0, 0, 0) is occupied by an atom and that other atoms must lie on the line $x=\frac{1}{2}, z=\frac{1}{2}$. The y coordinates of all these atoms could be found by calculating $P(\frac{1}{2}, y, \frac{1}{2})$, for there will be a maximum in this function at each value of y occupied by one of these atoms. Such examples could be multiplied almost indefinitely.

It is plain from the discussion above that the function $P(x, y, z)$ furnishes a powerful and simple method of attack on the structures of all crystals not belonging to the triclinic class. All that is required is a complete set of x-ray diffraction data, for from these not only can the symmetry of the crystal be determined, but also the values of $|F_{(hkl)}|^2$ calculated.

An illustration of the use of $P(x, y, z)$ is furnished by the determination of the structure of the mineral proustite, Ag_3AsS_3, which will be described below.

Determination of the Structure of Proustite, Ag_3AsS_3

The proustite used in this determination came from Schneeberg in Saxony. It occurred in the form of tiny, brilliant red, hexagonal prisms measuring about 0.2 mm by 1.0 mm which were bounded by beautiful faces.

Groth[2] describes proustite as ditrigonal pyramidal (C_{3v}) with the axial ratio $c/a=0.8038$. The density varies among different specimens from 5.55 to 5.62. This assignment to a polar class is made on the basis of many observations of unsymmetrical face development and seems exceptionally well grounded.

A Laue photograph taken perpendicular to a prism face showed a twofold axis of symmetry, another Laue photograph taken along a line bisecting the angle between two prism faces and perpendicular to the prism axis showed a plane of symmetry parallel to the prism axis, and a third Laue photograph taken along the prism axis showed a threefold axis and three planes of symmetry. The Laue symmetry is therefore D_{3d} and the crystal must belong to one of the point groups C_{3v}, D_3, or D_{3d} on the basis of x-ray data alone.

Measurements on oscillation photographs led to the dimensions $a_0=10.74$A, $c_0=8.64$A for the hexagonal unit cell. The ratio $c_0/a_0=0.804$ is in excellent agreement with the ratio $c/a=0.8038$ obtained from crystallographic measurements. The two Laue photographs taken perpendicular to the prism axis were indexed by the aid of gnomonic projections and the wave-length of the radiation producing each reflection calculated.

[2] P. Groth, Chemische Kristallographie, Vol. II, p. 767.

It was then found that no planes reflected in the first order unless the indices satisfied the condition imposed by the rhombohedral lattice, $2H+K+L=0 \bmod 3$, although many planes not satisfying this condition were in position to give first-order reflections. The lattice is consequently rhombohedral and its unit cell has one-third the volume of the hexagonal cell for which dimensions are recorded above. It is impossible to account for much of the observed data on the basis of a unit cell smaller than this and no data requiring a larger one has been found, although several hundred reflections on various photographs have been indexed. This rhombohedral cell is therefore the true unit cell of proustite. For convenience, however, the hexagonal cell will be used throughout this paper, much of the analytic geometry of the structure appearing simpler when referred to these axes. The limits of density given above require the number of formulas of Ag_3AsS_3 in the hexagonal unit cell to lie between 5.89 and 5.96. There are thus $6Ag_3AsS_3$ in this cell.

Determination of the Space Group

No reflections of the type $(OK\cdot L)$, L odd, were observed in the first order on any photograph, although many planes of this type were in position to reflect on both the Laue and oscillation photographs. There are two space groups based on the rhombohedral lattice which require this absence: $C_{3v}{}^6-R3c$ and $D_{3d}{}^6-R\bar{3}c$. The hemihedral face development of proustite eliminates the latter. Consequently the space group of proustite is $C_{3v}{}^6-R3c$.

Determination of the Structure

The space group $C_{3v}{}^6-R3c$ furnishes the following sets of equivalent positions:

(2a) $0, 0, Z$; $0, 0, Z+\frac{1}{2}$;

and (6b) X, Y, Z; $\bar{Y}, X-Y, Z$; $-X+Y, \bar{X}, Z$;

$X, X-Y, Z+\frac{1}{2}$; $\bar{Y}, \bar{X}, Z+\frac{1}{2}$; $-X+Y, Y, Z+\frac{1}{2}$;

and positions derived from these by the operations of the rhombohedral lattice.

There are 2 As, 6 Ag and 6 S atoms to distribute among these positions. The arsenic atoms must be placed in (2a) and the parameter Z_{As} may be arbitrarily taken to be zero. The arsenic atoms are now fixed at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$ in the hexagonal cell and the positions derived from these by the operations of the rhombohedral lattice. The silver and sulfur atoms must be in the general positions (6a) and there are consequently six parameters to be determined: X_{Ag}, Y_{Ag}, Z_{Ag}, and X_S, Y_S, Z_S.

In order to determine these parameters, the Patterson method described in the previous section was applied. The crystal contains a glide plane and so it is necessary to evaluate the Patterson function, $P(X, Y, Z)$, for points along a line only, in order to determine the distances of the atoms from the plane. By subtracting the coordinates of points produced from each other by the action of the glide plane perpendicular to the Y axis, it was found that there would be maxima in $P(X, Y, Z)$ at $(0, \pm(X-2Y), \frac{1}{2})$; $(0, \pm(-2X+Y), \frac{1}{2})$; $(0, \pm(X+Y), \frac{1}{2})$; for each kind of atom in the crystal. It was, therefore, only necessary to evaluate $P(0, Y, \frac{1}{2})$ in order to determine X and Y for each atom. Now

$$P(0, Y, \tfrac{1}{2}) = \sum_{H=-\infty}^{\infty} \sum_{K=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} |F_{HK\cdot L}|^2 \times \cos 2\pi(KY+L/2)$$

$$= \sum_{K=-\infty}^{\infty} C_K \cos 2\pi KY$$

with $$C_K = \sum_{H=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} (-1)^L |F_{HK\cdot L}|^2.$$

The coefficients C_K were calculated from the intensities of reflections on a series of oscillation photographs. A single small crystal was used throughout the series and all photographs were given the same exposure. The orientations of the crystal were so chosen that each possible reflection should have appeared near the equator on at least one of the series. The intensities of reflections were estimated by comparison with a series of spots of known exposure time on a strip of film, numbers proportional to the exposure times of the comparison spots being used to describe the intensities of the reflections. A complete search for reflections out to $(\sin\theta)/\lambda = 0.570$ was made, sixty-eight forms being observed to reflect within this limit. The intensities were divided by the

Lorentz and polarization factors in order to obtain the values of $|F_{HK\cdot L}|^2$. No corrections for extinction or absorption were made, as there was no way of estimating their effects.

The curve of $P(0,\ Y,\ \frac{1}{2})$ plotted against Y appears in Fig. 1. The large maximum at $Y=0$ is due, of course, to the vector between the arsenic atoms at (0, 0, 0) and (0, 0, $\frac{1}{2}$). The maxima at $\frac{1}{6}$, $\frac{1}{3}$ and $\frac{1}{2}$ were considered to be due mainly to the vectors between silver atoms, for the maxima due to vectors between sulfur atoms would be expected to be only about one tenth the size of these.

The axes can be so chosen that the inequalities $X_{Ag}+Y_{Ag}>2Y_{Ag}-X_{Ag}>2X_{Ag}-Y_{Ag}>0$ are satisfied. This choice and the positions of the maxima in $P(0,\ Y,\ \frac{1}{2})$ lead to the equations

$$X_{Ag}+Y_{Ag}=\tfrac{1}{2};\quad 2Y_{Ag}-X_{Ag}=\tfrac{1}{3};\quad 2X_{Ag}-Y_{Ag}=\tfrac{1}{6}.$$

These are solved by $X_{Ag}=4/18\leqq 0.22$ and $Y_{Ag}=5/18\leqq 0.28$. The silver atoms are now approximately located in the X, Y plane. The maxima in $P(0,\ Y,\ \frac{1}{2})$ are fairly broad and consequently the values of X_{Ag} and Y_{Ag} determined from these are not to be considered as accurate. However, a silver atom must lie near the line $X=4/18,\ Y=5/18$.

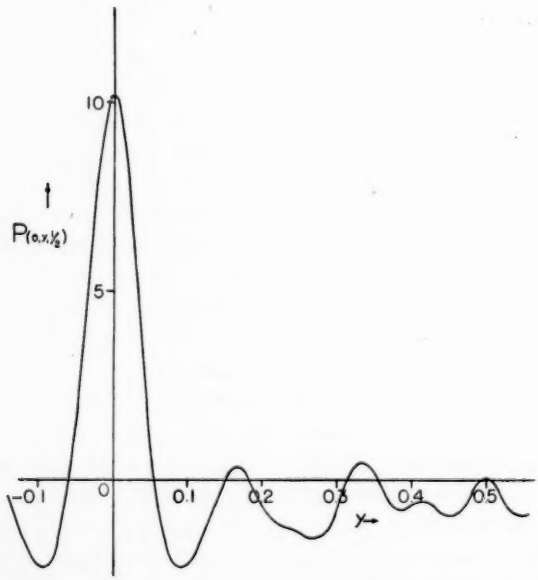

FIG. 1. $P(0,\ Y,\ \frac{1}{2})$ for proustite plotted against Y. The large maximum at $Y=0$ is due to As-As interaction, the maxima at 0.17, 0.33, and 0.50 are due to Ag-Ag interactions. There is a center of symmetry in $P(0,\ Y,\ \frac{1}{2})$ at $Y=\frac{1}{2}$, consequently only half the curve is plotted.

There is an arsenic atom at (0, 0, 0) and there must therefore be a maximum in $P(X,\ Y,\ Z)$ at $(X_{Ag},\ Y_{Ag},\ Z_{Ag})$. This maximum must lie near enough to the line $X=4/18,\ Y=5/18$ so that $P(4/18,\ 5/18,\ Z)$ should show a maximum at $Z=Z_{Ag}$. $P(4/18,\ 5/18,\ Z)$ was accordingly evaluated and the values plotted in Fig. 2 were obtained. The two sharp maxima at $Z=0.227$ and $Z=0.743$ can be due only to the vectors from the arsenic atoms at (0, 0, 0) and (0, 0, $-\frac{1}{2}$) to the silver atom. The values of Z_{Ag} calculated from the positions of these two maxima are $Z_{Ag}=0.227$ and $Z_{Ag}=0.243$. The mean of these is $Z_{Ag}=0.235$ with a probable error of about 0.008. The relation between the arsenic and silver atoms in the proustite structure is now approximately determined.

Hofmann[3] has stated that the AsS_3''' and SbS_3''' groups are pyramidal with bond angles of about 95° and bond lengths about equal to the covalent radius sums calculated from the table of Pauling and Huggins.[4] Corey and Wyckoff[5] in the study of $[Ag(NH_3)_2]_2SO_4$ and West[6] in the study of AgCN have shown that Ag′ forms two covalent bonds in opposed directions with a covalent radius of 1.36A. The assumption was accordingly made that the AsS_3''' groups in proustite were of approximately the form described by Hofmann and that silver atoms formed two covalent bonds to sulfur in opposed directions with a silver-sulfur distance of about 2.40A, which is the sum of the covalent radii. It was also assumed that sulfur would form bonds in approximately tetrahedral directions. It was found that these conditions could all be satisfied approximately by placing the sulfur atoms in proustite in the general positions (6a) with $X_S\leqq 0.22,\ Y_S\leqq 0.11,\ Z_S\leqq 0.40$. The complete structure of proustite was then roughly known.

The parameters X_{Ag} and Y_{Ag} were next fixed accurately by means of the intensities of the reflections $(HH\cdot 0)$, $H=1, 2, 3, 4, 5, 6$; assuming the sulfur positions as above. These intensities are as follows:

H	1	2	3	4	5	6
Observed Intensity of $(HH\cdot 0)$	0.50	0.40	0.45	0.10	0.15	0.20

[3] W. Hofmann, Zeits. f. Krist. **92**, 161 (1935).
[4] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).
[5] R. B. Corey and R. W. C. Wyckoff, Zeits. f. Krist. **87**, 264 (1934).
[6] C. D. West, Zeits. f. Krist. **90**, 555 (1935).

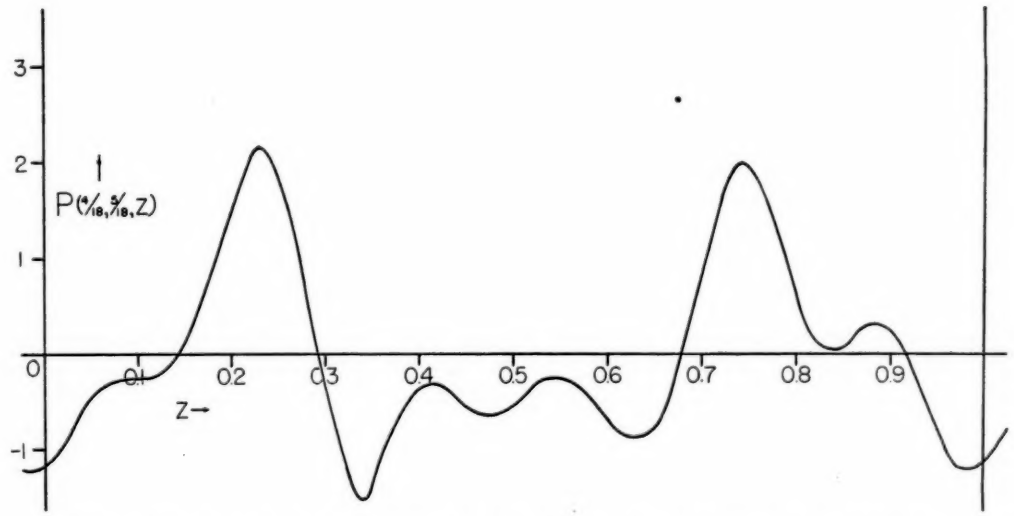

FIG. 2. $P(4/18, 5/18, Z)$ for proustite plotted against Z. The two large maxima are due to As-Ag interactions.

Fig. 3 shows the values of X_{Ag} and Y_{Ag} ruled out by the various comparisons. The center of the allowed region is at $X_{Ag}=0.246$, $Y_{Ag}=0.298$, and these values give calculated intensities in good agreement with the quantitative data with the sulfur parameters anywhere near $X_S=2/9$, $Y_S=1/9$. A change in X_{Ag} or Y_{Ag} of 0.005 in either direction places the point X_{Ag}, Y_{Ag} at, or beyond, the edge of the allowed region as shown in the figure. The limits of error in the determination of X_{Ag} and Y_{Ag} are consequently ± 0.005. If the Patterson method determination of Z_{Ag} is accepted, the silver parameters are now completely determined. The silver positions were accordingly assumed to be accurately known and the sulfur atoms placed so as to be 2.25A from arsenic atoms and 2.40A from silver atoms, these being the distances calculated from the covalent radii of these elements. The structure of proustite is now completely determined. The parameters are as follows:

$$X_{Ag}=0.246\pm0.005, \qquad X_S=0.220\pm0.10,$$
$$Y_{Ag}=0.298\pm0.005, \qquad Y_S=0.095\pm0.10,$$
$$Z_{Ag}=0.235\pm0.008, \qquad Z_S=0.385\pm0.10,$$
$$Z_{As}=0.000.$$

Intensities of all reflections for which $(\sin\theta)/\lambda \leqq 0.375$ were calculated and compared with the observed data. The results of this calculation appear in Table II. The agreement between the observed and calculated values proves the structure of proustite described above to be correct.

The structure of proustite being known, it is possible to discuss the positions at which maxima should fall in $P(0, Y, \frac{1}{2})$ and $P(4/18, 5/18, Z)$. Sulfur to sulfur distances should give maxima in $P(0, Y, \frac{1}{2})$ at $Y=0.030$, 0.315 and 0.345 corresponding to X_S-2Y_S, X_S+Y_S and $2X_S-Y_S$,

TABLE II. *Observed and calculated intensities for proustite.* In each square the top row gives the indices, and in the second row the first figure is the observed, the second figure is the calculated intensity.

		(12·5) 0.9 −0.87	(31·5) 0.45 −1.02		(23·5) 0.15 −0.45					
(10·4) 0.7 −1.93	(02·4) 1.3 −1.00	(21·4) 1.3 −0.71	(13·4) 1.2 −1.55	(40·4) 0.9 −1.48	(32·4) 0.10 −0.22	(05·4) 0.10 −0.42	(24·4) 0.15 −0.49			
	(11·3) 4.0 −4.39		(22·3) 0.25 −0.17		(14·3) 0.30 −0.13	(41·3) 0.25 −0.15	(33·3) 0.25 −0.05	(25·3) 0.15 −0.37	(52·3) 0.15 −0.29	
(01·2) 0.40 −0.16	(20·2) 4.5 −2.86	(12·2) 2.5 −1.97	(31·2) 1.0 −0.60	(04·2) 0.30 −0.20	(23·2) 1.3 −1.40	(50·2) 1.2 −1.22	(42·2) 0.45 −0.62	(15·2) 0.40 −0.33	(34·2) 0.10 −0.14	(61·2) 0.15 −0.14
		(21·1) 1.5 −1.51	(13·1) 2.0 −1.79		(32·1) 0.8 −0.77		(24·1) 0.40 −0.53	(51·1) 0.00 −0.07	(43·1) 0.30 −0.37	(16·1) 0.15 −0.12
	(11·0) 0.50 −0.35	(03·0) 1.8 −1.71	(22·0) 0.40 −0.10		(41·0) 0.40 −0.22		(33·0) 0.45 −0.24	(06·0) 0.60 −1.20	(52·0) 0.40 −0.54	(44·0) 0.10 −0.04

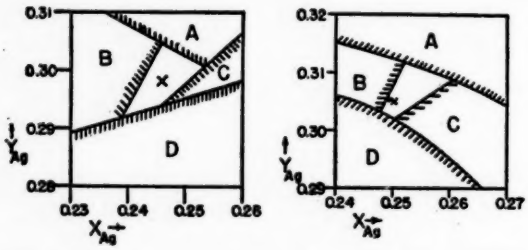

FIG. 3. (left) Determination of X_{Ag} and Y_{Ag} for proustite using comparisons of intensities of reflections $(HH\cdot 0)$.

Region A is ruled out by $I(55\cdot 0)$ calc. $> I(66\cdot 0)$
" B " " " " $I(22\cdot 0)$ " $> I(33\cdot 0)$
" C " " " " $I(44\cdot 0)$ " $> I(22\cdot 0)$
" D " " " " $I(44\cdot 0)$ " $> I(55\cdot 0)$

X marks the point giving the best quantitative agreement.

FIG. 4. (right) Determination of X_{Ag} and Y_{Ag} for pyrargyrite by comparisons of intensities of reflections $(HH\cdot 0)$.

Region A is ruled out by $I(66\cdot 0)$ calc. $< \frac{1}{4} I(55\cdot 0)$
" B " " " " $I(22\cdot 0)$ " $> I(33\cdot 0)$
" C " " " " $I(44\cdot 0)$ " $> \frac{1}{4} I(22\cdot 0)$
" D " " " " $I(66\cdot 0)$ " $> I(55\cdot 0)$

X marks the point giving the best quantitative agreement.

respectively, silver to silver distances should give maxima at $Y=0.194$, 0.350, 0.456 and 0.544 corresponding to $2X_{Ag}-Y_{Ag}$, $2Y_{Ag}-X_{Ag}$, $1-X_{Ag}-Y_{Ag}$ and $X_{Ag}+Y_{Ag}$ respectively, and arsenic-arsenic distances account for a maximum at $Y=0$. No other interatomic vectors should give maxima in $P(0, Y, \frac{1}{2})$. Comparing these figures with the curve for $P(0, Y, \frac{1}{2})$ in Fig. 1, it is seen that the maximum at $Y=0$ must be due to an As–As and a S–S distance, that at $Y=0.17$ must be due to a Ag–Ag distance, that at $Y=0.33$ must be due to two S–S and one Ag–Ag distance, and that at $Y=0.50$ to two Ag–Ag distances. The small maxima at $Y=0.25$ and $Y=0.41$ are not accounted for by any interatomic vectors and must consequently be due to the background fluctuation which occurs in any Fourier series treatment using only a finite number of terms. The small maxima in $P(4/18, 5/18, Z)$ (see Fig. 2) must be due to this same background effect as only the Ag–As vectors should produce maxima in this function.

THE CRYSTAL STRUCTURE OF PYRARGYRITE Ag_3SbS_3

The pyrargyrite used in this study was from Freiberg in Saxony and occurred in the form of metallic appearing, hexagonal prisms measuring about 0.5 mm by 2.0 mm.

Groth[2] assigned pyrargyrite to the ditrigonal pyramidal class (C_{3v}) with the axial ratio $c/a=0.7892$. The density ranges from 5.75 to 5.85. In this case, as in the case of proustite, the assignment to the polar class C_{3v} is well grounded on observations of unsymmetrical face development.

Measurements of reflections on oscillation photographs led to the axial lengths $a_0=11.04$A, $c_0=8.71$A for the hexagonal unit cell. The axial ratio is $c_0/a_0=0.789$, in good agreement with the ratio $c/a=0.7892$ calculated from crystallographic measurements. The number of formulas of Ag_3SbS_3 in this unit cell was calculated from the density range given above to lie between 5.92 and 6.03. There are thus 6 formulas of Ag_3SbS_3 in the unit cell.

Both the Laue and oscillation photographs of pyrargyrite show great similarity to the corresponding photographs of proustite. In particular, the conditions required by the rhombohedral lattice and the space group $C_{3v}{}^6-R3c$ were never violated. These observations, together with the

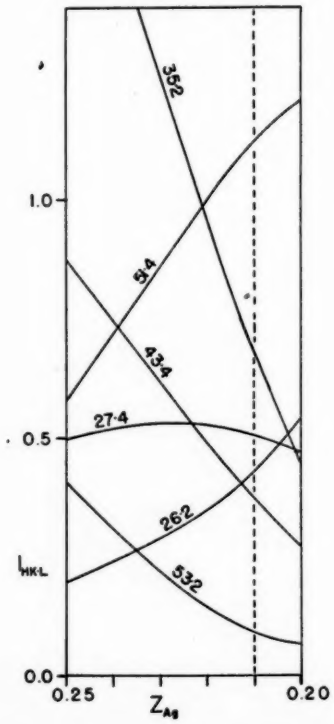

FIG. 5. Determination of Z_{Ag} for pyrargyrite by comparisons of intensities. $I_{HK\cdot L}$ plotted on an arbitrary scale against Z_{Ag}. The dotted line shows the chosen value. The observed intensities satisfy the inequalities: $I(51\cdot 4) > I(35\cdot 4) > I(27\cdot 4) > I(26\cdot 2) > I(43\cdot 4)$.

similarity between the chemical compositions, crystallographic data, and unit cell dimensions of pyrargyrite and proustite, led to the assumption that these two substances have nearly the same structure, the chief difference being the substitution of the arsenic atoms in proustite by antimony atoms in pyrargyrite. That this assumption was justified is amply proved by the agreement between the calculated and observed intensities of reflection which resulted from its adoption.

Gossner and Mussgnug[7] made layer line measurements on oscillation photographs of pyrargyrite from which they determined the lengths of the hexagonal axes to be $a_0=11.06$A and $c_0=8.84$A in good agreement with the results obtained in this research. They also proved the lattice to be rhombohedral and determined the space group to be $C_{3v}{}^6-R3c$. They did not determine the structure, however.

The assumption that proustite and pyrargyrite have almost the same structure leads at once to the approximate structure for pyrargyrite:

$C_{3v}{}^6$; 2 Sb in 2*a*, $Z_{Sb}=0.000$; 6 S in 6*b* $X_S \leqq 0.22$, $Y_S \leqq 0.10$, $Z_S \leqq 0.40$.
6 Ag in 6*b*, $X_{Ag} \leqq 0.25$, $Y_{Ag} \leqq 0.30$, $Z_{Ag} \leqq 0.23$;

The silver parameters X_{Ag} and Y_{Ag} were determined, as in the case of proustite, by use of the intensities of the reflections $(HH\cdot 0)$, $H=1$ to 6. These intensities were as follows:

H	1	2	3	4	5	6
Observed Intensity of $(HH\cdot 0)$	0.0	5.0	6.0	0.40	1.5	0.80

The regions of variation of X_{Ag} and Y_{Ag} ruled out by the various comparison are shown in Fig. 4. Values of the parameters differing from $X_{Ag}=0.250$, $Y_{Ag}=0.305$ by as much as 0.005 gave poor agreement with the observed data, and these values were therefore accepted as being correct to ± 0.005. The parameter Z_{Ag} was determined by comparisons, some of which are shown in Fig. 5, to be within 0.005 of $Z_{Ag}=0.210$. The sulfur atoms were then placed so as to make the SbS_3''' groups pyramidal with the Sb–S distance 2.45A and the Ag–S distance 2.40A, in agreement with the covalent radii of these elements. The determination of the structure of pyrargyrite was then complete. The parameters are

$$X_{Ag}=0.250\pm0.005, \quad X_S=0.220\pm0.010,$$
$$Y_{Ag}=0.305\pm0.005, \quad Y_S=0.105\pm0.010,$$
$$Z_{Ag}=0.210\pm0.005, \quad Z_S=0.355\pm0.010,$$
$$Z_{Sb}=0.000.$$

Intensities were calculated on the basis of this structure for all the reflections for which calculations had been made for proustite.

The results of these calculations appear in Table III. The agreement between the observed and calculated intensities of reflection proves the above structure to be correct.

Discussion of the Structures of Proustite and Pyrargyrite

The structure of proustite is shown in Fig. 6, and the structure of pyrargyrite is so similar that this figure may be used for the discussion of both. Both structures contain $(AgS)_\infty$ groups of almost the same shape. In these, the sulfur atoms form the corners of a triangular spiral, while the silver atoms lie almost in the centers of the legs of the spiral. The sulfur to silver distance is 2.40A, the

[7] B. Gossner and F. Mussgnug, Centralbl. f. Min. (**A**), 65 (1928).

TABLE III. *Observed and calculated intensities for pyrargyrite.* In each square the top row gives the indices, and in the second row the first figure is the observed, the second figure is the calculated intensity.

		(12·5) 2.0 – 2.94	(31·5) 1.2 – 3.59		(23·5) 0.45 – 1.00					
(10·4) 10.0 – 12.50	(02·4) 3.0 – 1.09	(21·4) 6.0 – 5.56	(13·4) 7.0 – 6.04	(40·4) 4.5 – 5.65	(32·4) 0.00 – 0.40	(05·4) 0.00 – 0.42	(24·4) 2.0 – 2.82			
	(11·3) 12.0 – 15.37		(22·3) 0.9 – 1.08		(14·3) 0.45 – 0.40	(41·3) 0.45 – 0.43	(33·3) 0.50 – 0.44	(25·3) 0.60 – 0.68	(52·3) 0.45 – 0.69	
(01·2) 6.0 – 3.60	(20·2) 12.0 – 12.28	(12·2) 10.0 – 10.50	(31·2) 4.0 – 3.19	(04·2) 1.5 – 1.09	(23·2) 5.0 – 4.73	(50·2) 5.5 – 5.23	(42·2) 3.0 – 2.49	(15·2) 2.5 – 2.00	(34·2) 0.50 – 0.27	(61·2) 1.0 – 0.91
		(21·1) 5.0 – 5.79	(13·1) 5.5 – 6.66		(32·1) 2.0 – 1.61		(24·1) 1.5 – 1.82	(51·1) 0.00 – 0.19	(43·1) 1.3 – 1.29	(16·1) 0.7 – 0.80
	(11·0) 0.00 – 0.13	(03·0) 8.0 – 10.0	(22·0) 3.0 – 1.39		(41·0) 1.5 – 0.92		(33·0) 3.5 – 1.75	(06·0) 3.0 – 3.62	(52·0) 2.5 – 3.12	(44·0) 0.40 – 0.16

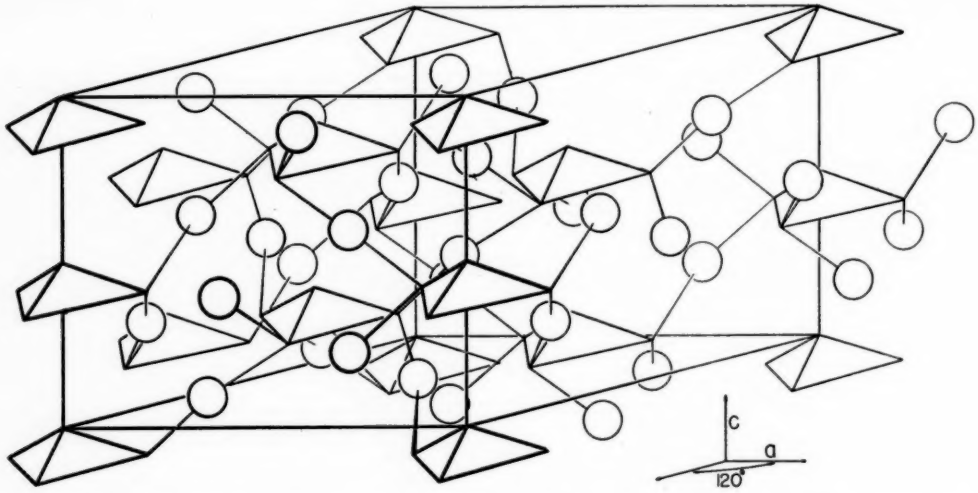

FIG. 6. The structure of proustite. Pyramids represent AsS_3''' groups, balls represent silver atoms, and lines represent covalent bonds. The structure of pyrargyrite is almost the same.

S−Ag−S bond angle is about 165°, and the Ag−S−Ag bond angle is about 83½°. One complete turn of the spiral is equivalent to a translation of c_0 in the crystal. These spirals are fastened together by the As or Sb atoms to make up the structural frameworks of proustite or pyrargyrite, respectively. The sulfur to arsenic bond distance in proustite is 2.25A and the S−As−S bond angle is 103°. The sulfur atom in proustite forms three bonds, two to silver and one to arsenic with these angles: As−S−Ag = 101° and 105½°, Ag−S−Ag = 83½°. In pyrargyrite the antimony atoms form three bonds to sulfur 2.45A long at mutual angles of 95½°. The sulfur atoms in pyrargyrite form three bonds with the angles: Sb−S−Ag = 97° and 111°, Ag−S−Ag = 83½°.

An interesting feature of these structures is the fact that they are composed of two interpenetrating frameworks of the type described in the last paragraph which are apparently not connected by any bonds at all. The relation of the two frameworks can best be understood by a study of Fig. 6. The As or Sb atoms at (0, 0, 0) belong to one framework and the crystallographically equivalent As or Sb atoms at (0, 0, ½) belong to the other. The two frameworks are in the relation to each other required by the operation of the glide planes. One framework contains only right-handed $(AgS)_\infty$ spirals, the other only left-handed ones. Another example of two interpenetrating frameworks apparently not interconnected by chemical bonds is furnished by the structure of cuprite, Cu_2O.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor Linus Pauling, who suggested the study of proustite and pyrargyrite, for sparing neither criticism nor encouragement throughout the course of this research.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Water Vapor Discharge and Hydrogen Peroxide Formation

The discharge (with or without electrodes) through water vapor may produce a mixture of the following molecules and atoms:

$$H, OH, H_2, O, O_2, H_2O\ (H_2O_2, HO_2, O_3).$$

Some years ago Geib and Harteck[1] showed that between 30°K to 150°K and at pressures of 0.1–0.5 mm Hg hydrogen atoms and molecular oxygen react on the walls without activation energy with 100 percent efficiency to give pure hydrogen peroxide. If however the temperature is raised to 190°K, rather poor yields of H_2O_2 are obtained. Thus we were astonished, when Rodebush and Wahl suggested that the formation of hydrogen peroxide in the electrodeless water vapor discharge was due to a bimolecular association of OH radicals. Recently I carried out experiments on this and using an electrode discharge I got the following results:

Large quantities of H_2O_2 are collected in a trap cooled with liquid air both in the water vapor discharge and in the discharge through H_2, O_2 mixture. On the other hand, if the products are frozen out at −80°C both in the discharge tube itself and 10 cm from it, not a singie drop of N/10 $KMnO_4$ solution is needed to oxidize the hydrogen peroxide.

These results now are an excellent agreement with those of Rodebush and Campbell,[2] who used an electrodeless discharge.

As the result of all experiments it must be stated: (1) It is quite unimportant whether or not electrodes are used; (2) Hydrogen peroxide is formed by the products of the water vapor discharge only at temperatures below −100°C; (3) Hydrogen peroxide is formed by a mixture of H atoms and molecular oxygen and a mixture of H atoms and O atoms at temperatures below −100°C; (4) H atoms are destroyed by adsorption and recombination at a glass surface cooled with liquid air, but not with solid carbon dioxide.[3]

This suggests the following mechanism[3] of hydrogen peroxide-formation

$$W+H \rightleftarrows WH, \quad W = \text{wall (glass surface, } H_2O \text{ or } H_2O_2);$$

$$WH+O_2 \rightarrow WHO_2;$$

$$WHO_2+H \rightarrow W+H_2O_2.$$

It seems rather difficult to show, that beside this process the recombination of OH radicals to H_2O_2 plays an important role (perhaps also as wall reaction) in the formation of H_2O_2, as Rodebush and Wahl[4] suggest. Experiment only shows that no such formation can be detected at temperatures above −100°C at low pressures.

In this connection one should discuss again both the reaction

$$H+H_2O_2 \rightarrow H_2O+OH^3$$

and the Bonhoeffer and Pearson mechanism[5]

$$2OH \rightarrow H_2O+O,$$

assigning to the latter some activation energy because of the work of Oldenberg.[6]

Rodebush and Wahl don't find O atoms[7] in their experiments. Possibly they react very fast, perhaps at every 10th collision, with OH to O_2+H.

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Physikalisch-Chemisches Institut der Universitat Leipzig
April 22, 1936.

[1] Geib and Harteck, Ber. d. D. Chem. Ges. **65**, 1551 (1932); Zeits. f. physik. Chemie **A170**, 1 (1934).
[2] Campbell and Rodebush, J. Chem. Phys. **4**, 293 (1936).
[3] Geib, Zeits. f. physik. Chemie **A169**, 161 (1934).
[4] Rodebush and Wahl, J. Chem. Phys. **1**, 696 (1933).
[5] Bonhoeffer and Pearson, Zeits. f. physik. Chemie **B14**, 5 (1931).
[6] Oldenberg, J. Chem. Phys. **3**, 266 (1935).
[7] See Oldenberg, reference 6, p. 273.

Entropy of Organic Compounds from Calorimetric Data. Lack of Equilibrium in Crystalline Tetramethylmethane

Recently Kassel[1] has calculated the entropy of *n*-butane from spectroscopic data and found a value 3.76 e.u. higher than that of Huffman, Parks and Barmore[2] which he suggests may be due to lack of equilibrium in the solid at low temperatures or to an error in the value extrapolated below 90°K. As the total extrapolated value is only 11.7 e.u., it is hardly possible that the error could be due to this cause unless a transition of rather large entropy change were involved.

We have recently measured the entropy difference between ordinary crystalline tetramethylmethane at the absolute zero and the gas at 25°C from calorimetric measurements carried down to 14°K, the extrapolated entropy being only 0.66 e.u. While the calculations are not entirely complete a comparison of a preliminary value of this calorimetric entropy difference with the entropy of the

gas at 25°C shows the calorimetric value to be about 8 e.u. lower than the spectropscopic value. This indicates about 8 e.u. zero-point entropy in the ordinary crystal of tetramethylmethane at the absolute zero, due to randomness caused by lack of equilibrium. There is an abnormal rise in the heat capacity of the solid prior to a transition at 140°K. In this region only is there evidence of hysteresis.

Giauque and associates have found a similar state of affairs for carbon monoxide[3a] and nitrous oxide[3b] and predicted the occurrence of the phenomenon in the case of organic compounds. Pauling has discussed the situation for some simple molecules.[4]

In view of the large discrepancy in the case of tetramethylmethane one must view entropies of organic compounds calculated from calorimetric data assuming a perfect crystal (i.e., zero entropy at the absolute zero) with considerable doubt even though they be based on heat capacities taken down to liquid hydrogen temperatures or lower.

At present the only source of a reliable value or the entropy of neopentane is a calculation based on spectroscopic data and a knowledge of the moments of inertia. Such a calculation yields a value of 79.85 e.u. at 25° and 1 atmos. neglecting nuclear spin. This value is the translational and rotational entropy 73.98 e.u.[1] plus the entropy of vibration (5.87 e.u.) calculated from the Raman frequencies determined by Rank and Bordner,[5] using the following multiplicities: 335, (2); 414, (3); 733, (1); 925, (3).

The complete calorimetric data will be submitted for publication in the near future.

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The Pennsylvania State College,
State College, Pennsylvania,
April 23, 1936.

[1] Kassel, J. Chem. Phys. **4**, 277 (1936).
[2] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[3a] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).
[3b] Blue and Giauque, ibid. **57**, 991 (1935).
[4] Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).
[5] Rank and Bordner, J. Chem. Phys. **3**, 248 (1935).

The Raman Effect and the Dissociation of $KHSO_4$

It has been found by Rao[1] and others that a study of the Raman effect offers a means of determining the degree of dissociation of concentrated solutions, where other methods are not applicable, and thus supplies valuable information with respect to the physical and chemical properties of such solutions. Woodward,[2] Nisi,[3] and Bell and Jeppesen[4] have observed the Raman effect in $KHSO_4$ at one concentration but made no observations on the change in the degree of dissociation with the concentration.

They found that $\bar{H}SO_4$ ions occur in a concentrated aqueous solution of $KHSO_4$ and that these ions partially dissociate into $\dot{H}$ and $\bar{\bar{S}}O_4$. This is precisely what might be expected from chemical considerations which indicate that $KHSO_4$ would dissociate in two stages:

$$KHSO_4 \rightarrow \dot{K} + \bar{H}SO_4; \quad \bar{H}SO_4 \rightarrow \dot{H} + \bar{\bar{S}}O_4.$$

Since other studies of the Raman effect in concentrated solutions indicate that normal salts are completely dissociated at all concentrations, and that in strong acids the degree of dissociation increases with dilution, it is of interest to consider what happens in the Raman spectrum of an acid salt like $KHSO_4$ when the concentration of the solution is changed.

By means of a high speed spectrograph of low dispersion the Raman effect was photographed in four aqueous solutions of $KHSO_4$ of the following concentrations: 13, 21, 28, 34 percent. The solutions were enclosed in the usual type of Wood tube and illuminated by mercury arc lamps. The Raman spectra were excited by the 4358A and 4047A lines. The frequencies of the observed Raman lines expressed in wave numbers (cm^{-1}) for concentrations of 13 percent and 34 percent have been recorded in Table I.

TABLE I.

CONCENTRATION	$\bar{H}SO_4$	$\bar{H}SO_4$	$\bar{\bar{S}}O_4$	—	—
13%	1058	917	978	611	438
34%	1040	906	975	599	436

The ions to which these observed Raman lines have been attributed are indicated by the headings of the columns in the table. There is a change in frequency of the Raman lines with the dilution of the solution. A similar effect has been observed by Woodward and Horner[5] and also by Bell and Jeppesen[4] in the case of aqueous solutions of H_2SO_4. The reality of such a change in frequency due to a change in concentration has been questioned by Mitra[6] but his observations on aqueous solutions of magnesium sulphate and lithium sulphate were concerned only with the Raman line 981 cm^{-1} which has been attributed to $\bar{\bar{S}}O_4$. For this line the change in frequency due to the change in the concentration of the solution is small compared to the changes observed for the other lines.

From a comparison of the intensities of the Raman lines as indicated by the microphotometer curves, the relative degrees of dissociation of the solutions with respect to the

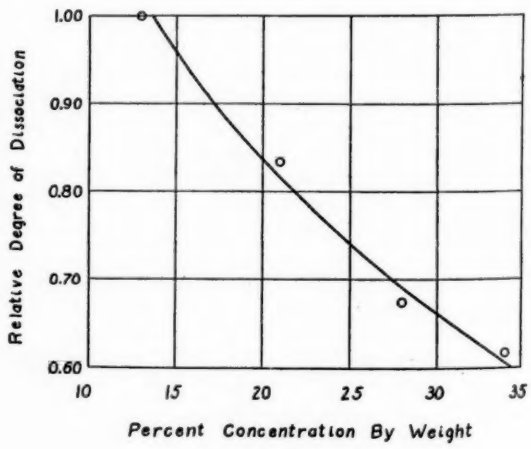

FIG. 1

degree of dissociation of 13 percent solution have been calculated and recorded in Table II. These results are also

TABLE II.

PERCENT CONCENTRATION	13	21	28	34
RELATIVE DEGREE OF DISSOCIATION	1.00	0.84	0.68	0.82

shown as a curve (Fig. 1) with the degree of dissociation plotted against the concentration. From this curve the progressive dissociation of the HSO_4^- ion is clearly seen. No lines attributable to the undissociated $KHSO_4$ molecule were observed even in the most concentrated solution. The fact that no undissociated molecules are present in solution is characteristic of normal salts, while the fact that the HSO_4^- ion dissociates progressively is characteristic of acids. Thus the Raman method of investigation indicates that $KHSO_4$ has characteristics common to both acids and normal salts as would be inferred from chemical considerations.

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Quantum Mechanics and the Third Law of Thermodynamics

Rodebush[1] has recently discussed certain points concerning the third law of thermodynamics in terms of quantum mechanics. His recognition of the significance of quantum mechanics in considering the behavior of solutions and glasses at low temperatures we believe to be of interest, and we agree with the more important of his conclusions. However, there have arisen some questions of interpretation in which we differ from the statements of his paper. We have thought it of value to present here, as explicitly as possible and at the risk of some duplication of ideas, an outline of these points and a discussion of their bearing on the expected behavior of the systems under treatment. It is our opinion that the views presented below have been in the main accepted by investigators interested in the theory of the third law; however, so far as we are aware no equivalent discussion has been published.

Without entering into the question of the relation between statistical mechanics and thermodynamics, we accept as giving a value for the entropy of the system in which we are interested the expression $k \ln N$, in which N is the number of independent wave functions for the system compatible with our knowledge as to its condition. Following the plan adopted by Rodebush, we first discuss the case of an optically active substance.[2] An isolated molecule of such a substance in its lowest rotational and vibrational state and known to be in the dextro configuration[3] is to be represented by a single wave function corresponding to this configuration, and will have the quantum weight 1, and not 2. On the other hand, if the molecule is in one of the two lowest energy states corresponding to the accurate solution of the wave equation (as could be determined by an energy measurement extending over a period of time long compared to the time required for spontaneous dextro-levo conversion), it is to be represented by a single wave function which is either symmetric or antisymmetric relative to inversion about a center, and which is formed by linear combination of the dextro and levo wave functions. It will then not be known whether the molecule is a dextro or a levo molecule. Only in the case that neither its optical activity nor its (exact) energy is known can we assign to it the quantum weight 2.

By analogy with the simple case of the optical isomers Rodebush generalizes the many-minima problem exemplified by glasses and crystalline solutions with the following statement. "We have a number of configurations of the same energy separated by energy crests. By symmetric and antisymmetric linear combinations of wave functions,[4] we obtain a total number of wave functions equal to the degeneracy; that is to say, the total number of configurations having the same energy. Thus, instead of each configuration having a distinct energy, each configuration has now a large number of closely spaced energy levels."

Here we prefer to state the situation in a somewhat different way, as follows. The system in its low temperature condition and known to have a particular configuration[5] (one of N possible configurations) is to be represented by one of an appropriate set of N wave functions, corresponding to the N configurations. If not the configuration, but the energy of the system is to be investigated with great accuracy, by means of observations extending over a very long period of time, the set of wave functions of interest is that corresponding to accurate solution of the wave equation (these wave functions being linear combinations of those corresponding to the N configurations). The energy value found by experiment would be one of the multiplet of N levels corresponding to the low temperature condition. We cannot, however, make use of the two sets of wave functions simultaneously, but must use either the configuration wave functions or the multiplet wave functions, or some other equivalent set. In other words, both the configuration and the exact energy of the system cannot be simultaneously known. If either is known a single wave function (of the set of N) is sufficient to describe the system and the system will then have the quantum weight 1, and not N. However, if neither the configuration nor the exact energy of the system is known, we may use either set of N wave functions (or any other set formed from them by linear combinations) to describe it, and its quantum weight will then be N.

The behavior of systems on cooling to a very low temperature ($kT \ll h\nu$, where ν is the frequency of the lowest oscillational state) may be outlined in the case of an ideal solution somewhat as follows.[6] If ν^* is the frequency of transition among the various configurations (as given by the corresponding resonance integral divided by h), the

energy spread of the multiplet levels will be of the order of $h\nu^*$. If the cooling be done so slowly that a time very long compared to $1/\nu^*$ is allowed at each temperature, the loss of heat will be such as to correspond to a loss of entropy of $k \ln N$, since the multiplet levels under such conditions may be regarded as discrete. On rapid cooling to the same low temperature, the energy of the system will be determinable only to within about $h/2\pi\tau$, where τ is the time of observation at the temperature in question. If this uncertainty in energy is large compared to $h\nu^*$ there will still remain N states (N independent wave functions) of the system falling within the observable energy limits, and the entropy will be $k \ln N$. Only after a long time of observation at this temperature can these limits be narrowed sufficiently to permit the statement that a single state is represented and the entropy is zero.

A real solution or glass differs from an ideal solution or glass, discussed above, in that one of its configurations, corresponding to a pure crystalline substance or a mixture of pure crystalline substances, possesses an energy lower than any other. If such a system be subjected to very slow cooling, or be held for a long time at a low temperature as discussed above, it will ultimately attain this configuration (mainly by transition through excited vibrational states rather than by penetration of potential barriers), and will therefore have zero entropy. On cooling sufficiently rapidly to exclude effectively transitions between configurations, or on holding at the low temperature for a time shorter than required for these transitions to occur, the multiplicity N will be retained by the system, its entropy then remaining greater than zero.

It may be pointed out that the discussion of the entropy of a real solution or glass on the basis of quantum mechanics, as just given, is identical with the discussion of the problem in the pre-quantum-mechanical era. On the other hand, the quantum mechanics has introduced a significant change in the discussion of the entropy of an ideal solution or glass. Before the development of quantum mechanics there was no conceivable mechanism leading to the loss of the final $k \ln N$ of entropy at very low temperatures for an ideal solution or glass, defined as having N configurations with exactly the same energy. The quantum-mechanical mechanism leading to the loss of this entropy is the resonance of the system among the N configurations.

Rodebush has also implied that the accuracy with which very low temperatures can be measured is restricted by the uncertainty principle and by the nature of the substance under investigation. However, the accuracy of a temperature measurement is not limited in a serious way by the uncertainty principle for energy, inasmuch as the relation between the uncertainty in temperature and the length of time involved in the measurement depends on the size of the thermometer, and the uncertainty in temperature can be made arbitrarily small by sufficiently increasing the size of the thermometer; we assume as the temperature of the substance the temperature of the surrounding thermostat with which it is in either stable or metastable equilibrium, provided that thermal equilibrium effective for the time of the investigation is reached.

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[1] W. H. Rodebush, J. Chem. Phys. **2**, 669 (1934).
[2] For a thorough discussion of this see F. Hund, Zeits. f. Physik **43**, 805 (1927).
[3] We shall use the word configuration in this paper to represent the approximate relative spatial arrangement of the nuclei of the atoms in the system under consideration (neglecting the effect of the vibrational motion on the nuclear positions).
[4] At the request of Professor Rodebush, the wording of this sentence has been changed slightly from that in his paper.
[5] We assume each configuration to be in its lowest vibrational state.
[6] We believe that the ideas discussed in this connection parallel those of Rodebush, but have thought it worth while to give them in greater detail.